



ANGLO AMERICAN Geochemical Sampling and Analytical Protocols

Soils	
SOP Number: 1.60 Version 1	Date: September 30, 2001 Author: Christopher Oates, Vice-President, Geochemistry

NOTE: GOLD RINGS AND ALL JEWELLERY MUST BE REMOVED AND HANDS WASHED THOROUGHLY PRIOR TO COMMENCING ALL SAMPLING PROGRAMS

The objective is to collect representative soil samples. Contamination from equipment and cross-contamination from other samples must be eliminated.

Sieving

Dry Soils □ sieve to □250um at sample site
Wet soils □ ship to lab for drying and sieve to □250um
Chemical soils (clay-rich) □ collect bulk, pulverise at lab

Equipment and Supplies

- all field sampling equipment must be AApIc approved stainless steel or plastic sieve sets
- Estwing hoe pick or equivalent
- Kraft (heavy brown paper) 5 in x 3 in single gusset, wire tie closure, soil sample bags
- standards.

Sample Site

- record data as per project and country requirements (Hub Geochemist)

Sample Collection and Preparation at the Sample Site

- collect sample from 5 to 25 cm depth (remove surficial crust) except in wet climates where the sample is collected from directly below the surface organic layer
- For sampling remove the first 8-10cms of the area to be sampled over an area of approx 1m diameter to ensure no surface contamination as well as removing all the surface organic material. Dig over and mix very well the central 30-40cm of the cleared area to a depth of approx 25cm. After mixing very well, shovel and sieve (if appropriate) 3 pans full of soil to- 1.00mm. Place sample into a large plastic for further sieving and bulk sample storage. Note: After sampling always fill the hole and level the area sampled. In areas of farming, USE THE SAME PROCEDURE DO NOT DIG DEEPER HOLES, NOR SAMPLE FROM A GREATER DEPTH.

Quality Control Samples

- Field duplicates and control standards are both inserted at a rate of at least 3 in 100.
- collect same location field duplicates at a rate of at least 3 in 100, number field duplicates with the next consecutive number after the sample number for the duplicate site (i.e. 29 / 30, 59 / 60, 89 / 90)
- add 35-50 g of control standard to Kraft sample bags at a rate of at least 3 in 100, using the sample numbers in the series that end in 33, 66 and 99 etc. AapIc S-series standards (S1, S2, S3 etc.) must be always inserted at a rate of 1 to 3 in 100. Other standards and blanks can be inserted as required.

**QUALITY ASSURANCE/ QUALITY CONTROL OF
LITHOGEOCHEMICAL DATA**

PROJECT GC51: GEOCHEMICAL BASELINES – LOS BRONCES

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May 2011

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Centre for Environmental Policy

Executive Summary

A total of 1148 rock samples were collected from the Los Bronces region in several sampling campaigns between 2007 and 2009 (Table 1). Seven analytical techniques, undertaken by Acme Analytical Laboratories (Vancouver) Ltd were used to provide a comprehensive suite of element analytes for the samples as summarised in (Table 2).

Table 1: The number of samples analysed from Los Bronces regions

Campaign	Total Samples	Samples	Field Duplicates	Standards
Los Bronces	1148	1038	51 (5%)	59 (6%)

Table 2: A summary of analytical techniques used to provide elemental analytes data discussed within this report (undertaken by Acme Analytical Laboratories (Vancouver) Ltd. www.acmelab.com)

Code	Full Name of Analysis (Acme Laboratory)	Technique Used
4AWR	Group 4A Whole Rock by ICP	Sample analysed by ICP-emission spectrometry following a Lithium metaborate/tetraborate fusion and dilute nitric acid digestion
4BWR	Group 4B Total Trace Elements by ICP - MS	Rare earth and refractory elements are determined by ICP mass spectrometry following a Lithium metaborate/tetraborate fusion and nitric acid digestion of sample. In addition, a separate split is digested in Aqua Regia and analysed by ICP mass spectrometry to report precious and base metals e.g. Au, Ag, Cd
7TDA	Group 7 ICP & ICP-MS	Percentage level concentrations as determined by ICP emission spectrometry
1FMS	Group 1F-MS Ultratrace by Mass Spec	ICP Mass Spec analysis of a sample after Aqua Regia digestion for low to ultra low determination on soils, sediments and lean rocks
4ALO	Group 4A Whole Rock by ICP (Loss of Ignition)	Weight difference after ignition at 1000°C
4ALC	Group 4A Whole Rock by ICP (LECO)	Total Carbon and Sulphur analysis by LECO
G3B-MS	Group 3B & 3B-MS	A lead-collection fire-assay fusion for total sample decomposition, digestion of the Ag dore bead and ICP-MS analysis.

The QA/QC assessment of the rock data shows that the dataset is of high quality.

Standards

The accuracy of the data was assessed by analysing two standards; Altered Andesite Whole Rock and Alkali Olivine Basalt (OREAS 24P) secondary reference material (SRM). The accuracy for each analytical method was assessed.

A pass-fail criterion was established whereby an element passed if ≥ 3 analysed standard samples for each element outside $\pm 25\%$ of the mean for that standard.

Since the samples were analysed over three years, improvements in detection mean that detection limits vary between analytical batches for methods 4AWR, 4BR and 4ALO. Therefore, for QA/QC purposes, sample batches for these analytical methods have been grouped according to the detection limits achieved. The QA/QC result was then calculated by averaging the individual results of each group for each analytical method (Table 3).

Table 3: Summary of QA/QC accuracy results for two standards (Alkali Altered Andesite and Olivine Basalt), grouped according to analytical method

Analytical Method	Percentage of elements meeting QC criterion	
	Olivine Basalt	Alkali Altered Andesite
4AWR	96%	91%
4AWR (1)	100%	91%
4AWR (2)	92%	91%
4BWR	100%	98%
4BWR (1)	100%	95%
4BWR (2)	100%	100%
4BWR (3)	100%	100%
7TDA	100%	0%[‡]
1FMS	50%	80%
4ALO	50%	100%
4ALO (1)	100%	100%
4ALO (2)	0%	100%
4ALC	0%	N/A
G3B-MS	N/A	100%

The accuracy of 6 of the 7 analytical methods was evaluated using the Olivine Basalt and Alkali Altered Andesite standards (Table 3). The QA/QC for Olivine Basalt standards for elements analysed using G3B-MS (Au, Pt, Pd) was not performed for no certified values are available for this method. Similarly, the Alkali Altered Andesite standards for carbon and sulphur analysed using 4ALC were not evaluated for QA/QC as there no certified values for them using the 4ALC method.

Overall, the results of both standards suggest that all of the analytical methods used produce highly accurate data. However, care should be taken when using 4ALC results for Carbon and Sulphur as these were less satisfactory in the QA/QC analysis. This is probably because the values are 10x detection limit.

[‡]Although the 7TDA method appears not to satisfy the QC pass-fail criterion for the Alkali Altered Andesite standard, this was the result of the exceedance of two points and, in combination with the excellent results for the Olivine Basalt standard, the dataset is considered suitable for use.

Field Duplicates

Data were evaluated for precision by comparing duplicates against two pass-fail criteria:

- 1) An element passed if 90% of samples were within ± 25 of the percentage relative difference
- 2) The entire dataset passed if the average percentage relative difference of all analytes was $< \pm 25\%$

Table 4: Summary of QA/QC reproducibility results for duplicates, grouped according to analytical method

Analytical Method	Percentage of elements meeting first QC criterion	Percentage of elements meeting second QC criterion
	(1) % duplicates with $\geq 90\%$ samples within $\pm 25\%$ of percentage relative difference:	(2) Average of average percentage relative difference:
4AWR	45%	10%
4BWR	17%	14%
4ALO	0%	15%
1FMS	0%	25%
7TDA	N/A	N/A
4ALC	N/A	N/A
G3B-MS	N/A	N/A

For all of the analytical methods used to analyse Los Bronces rock samples, the percentage of duplicates with $\leq 10\%$ samples within $\pm 25\%$ of relative difference was low (Table 4). However, this is thought to reflect the inherent heterogeneity of rock samples rather than poor reproducibility of the sampling procedure.

All datasets for the 4AWR, 4BWR, 4ALO and 1FMS analytical methods met the second QC criterion as they all showed an average percentage relative difference less than $\pm 25\%$.

Overall, although the performance of the datasets under the first criterion was poor, the excellent performance against the second criterion indicates that this is the result of intrinsic heterogeneity of rock samples and overall the samples demonstrate a high level of reproducibility.

Summary of QA/QC Results

Rock samples were collected from the Los Bronces region in several campaigns between 2007 and 2009 and a total of 1148 samples were collected.

Table 2: A summary of analytical techniques used to provide elemental analytes data discussed within this report (undertaken by Acme Analytical Laboratories (Vancouver) Ltd. www.acmelab.com)

Campaign	Total Samples	Samples	Field Duplicates	Standards
Los Bronces	1148	1038	51 (5%)	59 (6%)

The QA/QC assessment of the rock data shows that the dataset is of a high quality.

Seven analytical techniques, undertaken by AcmeLabs (*Acme Analytical Laboratories (Vancouver) Ltd*) were used to provide a comprehensive suite of element analytes for the samples as summarised in (Table 2).

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7TDA	Group 7 ICP & ICP-MS	Percentage level concentrations as determined by ICP emission spectrometry
1FMS	Group 1F-MS Ultratrace by Mass Spec	ICP Mass Spec analysis of a sample after Aqua Regia digestion for low to ultra low determination on soils, sediments and lean rocks
4ALO	Group 4A Whole Rock by ICP (Loss of Ignition)	Weight difference after ignition at 1000°C
4ALC	Group 4A Whole Rock by ICP (LECO)	Total Carbon and Sulphur analysis by LECO
G3B-MS	Group 3B & 3B-MS	A lead-collection fire-assay fusion for total sample decomposition, digestion of the Ag dore bead and ICP-MS analysis.

The analytes measured by each technique are summarised in Table 5.

Table 5: Summary of analytical techniques and elements analysed

Analytical Method	Analytes
4AWR	SiO ₂ , Al ₂ O ₃ , MgO, Na ₂ O, K ₂ O, TiO ₂ , P ₂ O ₅ , MnO, Cr ₂ O ₃ , Ba, Sc
4BWR	Ce, Cs, Dy, Er, Eu, Ga, Gd, Hf, Ho, La, Lu, Nb, Nd, Pr, Rb, Sm, Sn, Sr, Ta, Tb, Th, Tm, U, V, W, Y, Yb, Zr
4ALO	Loss on Ignition
1FMS	Ag, As, Au, B, Be, Bi, Cd, Co, Cr, Cu, Ge, Hg, In, Li, Mo, Mn, Ni, Pb, Pd, Pt, Re, Sb, Se, Te, Tl, Zn
7TDA	Ni
4ALC	C, S
G3B-MS	Au, Pd, Pt

Standards

In order to evaluate the accuracy of each of the analytical methods used, two types of standards (secondary reference material (SRM)), Altered Andesite Whole Rock and Alkali Olivine Basalt (OREAS 24P), were used. These standards were inserted into each analytical run and the results compared against known performance gates using graphs.

Performance gates for the analytical methods were referenced for 66 analytes. Performance gates included:

- 1) the mean of the SRM
- 2) $\pm 25\%$ of the mean
- 3) ± 2 standard deviation of the mean
- 4) ± 3 standard deviation of the mean

Ideally, 95% of all samples should fall between ± 2 standard deviations (warning lines), with 99% between ± 3 standard deviations (failure lines). The standard suggests that a batch of analyses has failed to reach the level of accuracy required if one or more samples lie outside the failure lines (red) or data for more than two standards fall outside any warning line (orange) (Figure 1).

To allow for the intrinsic heterogeneity of rock samples (which have variability in their mineralogy and hence chemistry) an additional pass-fail criterion was established. An element passed if ≥ 3 analysed standard samples for each element were outside $\pm 25\%$ of the mean for that standard. Elements below the detection limit were excluded from evaluation because the results were not reliable.

Graphs for each standard show the analytical results for the secondary reference material (SRM) plotted against the order of analytes (Figure 1).

The samples were analysed over three years and improvements in detection limits over that time mean that detection limits vary between analytical batches for methods 4AWR, 4BR and 4ALO. Therefore, for QA/QC purposes, sample batches for these analytical methods have been grouped according to the detection limits used. The QA/QC results were then calculated by averaging the individual results of each group of analytical methods (Table 3).

Table 3: Summary of QA/QC accuracy results for two standards (Alkali Altered Andesite and Olivine Basalt), grouped according to analytical method

Analytical Method	Percentage of elements meeting QC criterion	
	Olivine Basalt	Alkali Altered Andesite
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4BWR (2)	100%	100%
4BWR (3)	100%	100%
7TDA	100%	0%[‡]
1FMS	50%	80%
4ALO	50%	100%
4ALO (1)	100%	100%
4ALO (2)	0%	100%
4ALC	0%	N/A
G3B-MS	N/A	100%

Olivine Basalt

The accuracy of 6 of the 7 analytical methods was evaluated using the Olivine Basalt standard (Figure 1). The standards for elements analysed using G3B-MS (Au, Pt, Pd) were not evaluated since there are no certified values for the standard using this method.

For the 4AWR, 4BWR and 7TDA analytical methods, an evaluation of accuracy using the Olivine Basalt standards showed that the majority of elements had $<\pm 10\%$ bias between their mean and the certified mean, with 96% or higher of elements satisfying the QC pass-fail criterion. The level of accuracy of these datasets is high (Table 3).

The 1FMS, 4ALO and 4ALC methods however showed a large percentage bias between their mean and the certified mean. For 1FMS and 4ALO 50% of elements satisfied the QC pass-fail criterion. Although this is lower than the 4AWR, 4BWR and 7TDA methods, it accurate enough for the data to be acceptable for use.

The QA/QC results for 4ALC were poor hence data determined by 4ALC does not mean the QC pass-fail criteria, because one sample exceeds the limits. On closer inspection, the majority of samples for this analytical method are below 10x the detection limit (the mean is 0.1 which is 10x the detection limit). Therefore, the failure reflects the number of results that are close to the detection limit. 10x the detection limit is a value, beneath which variability may be greater for certain analytical methods. Overall the data are very consistent and the dataset is considered acceptable for use. This was also the case in approximately half of the samples analysed by 4ALO. To improve the performance of these elements in future, a greater number of samples should be collected for analysis.

The Olivine Basalt standards suggested that the data shows high levels of accuracy.

Alkali Altered Andesite

The accuracy of 6 of the 7 analytical methods was evaluated using the Alkaline Altered Andesite standard (Figure 1). The standards for carbon and sulphur analysed using 4ALC were not evaluated because there are no certified values for Alkali Altered Andesite using this method.

The majority of the analytical methods (4AWR, 4BWR, 1FMS, G3B, 7TDA) evaluated using the Alkali Altered Andesite standard had $<\pm 10\%$ bias between their mean and the certified mean. Except for 7TDA, data for 80% or higher of elements satisfied the QC pass-fail criterion for all analytical methods (Table 3).

¹The 7TDA method does not appear to satisfy the QC pass-fail criterion because 4 samples fall outside of $\pm 25\%$ of the mean. However, two of these samples exceed the limits by only 1ppm and there is $<\pm 10\%$ bias between the mean and the certified mean for the element analysed using this method.

Therefore data for the Alkaline Altered Andesite standards suggested that the data is highly accurate.

Overall, both standards suggest that all of the methods used produce highly accurate data. However, care should be taken when using 4ALC results for Carbon and Sulphur because results were poor, probably as a result of the values being close to 10x detection limit.

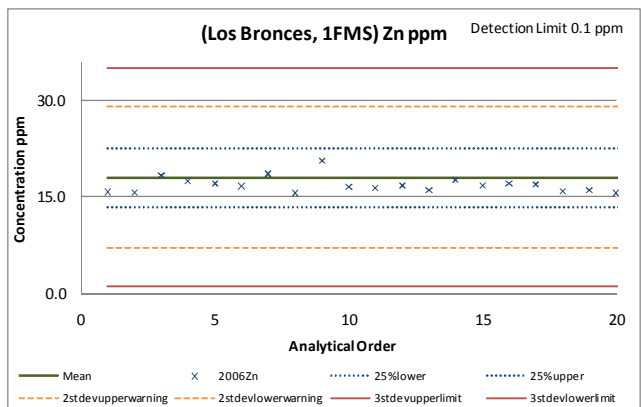
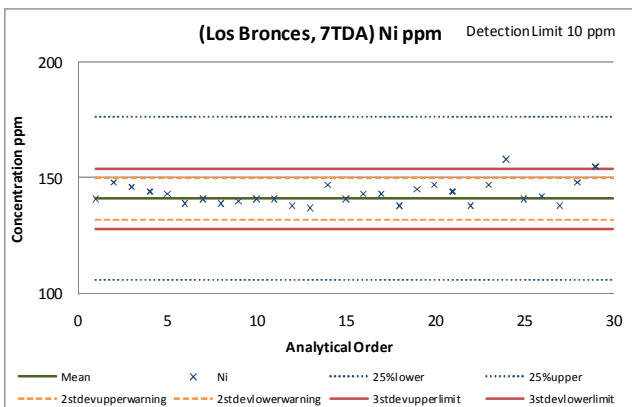
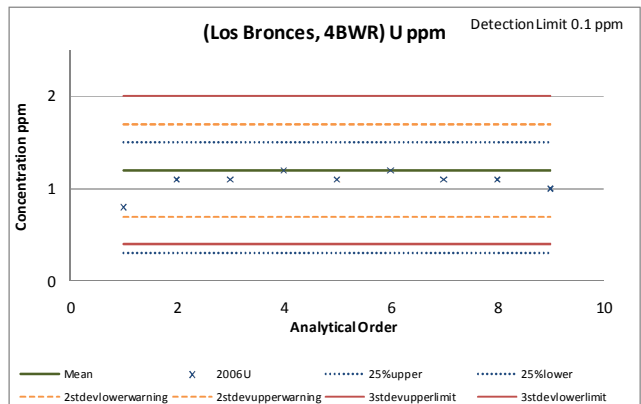
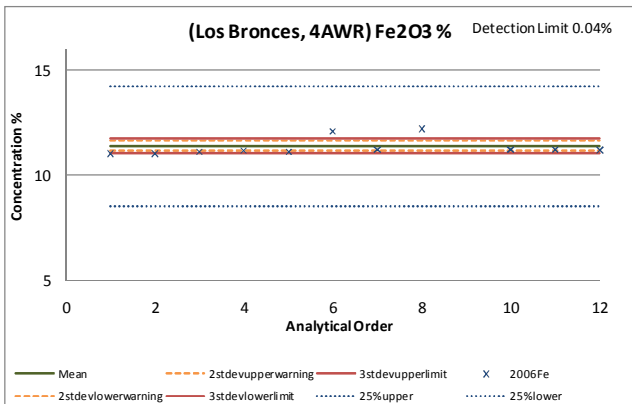
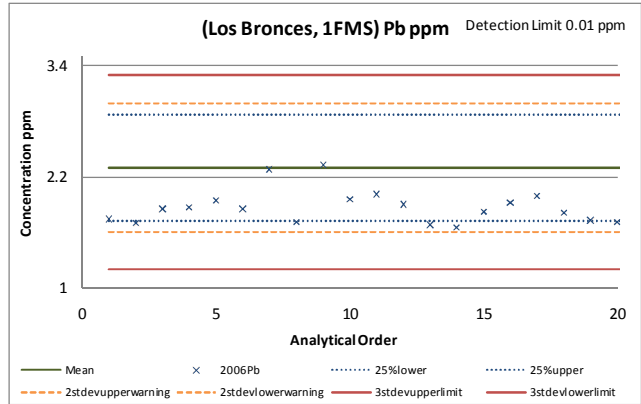
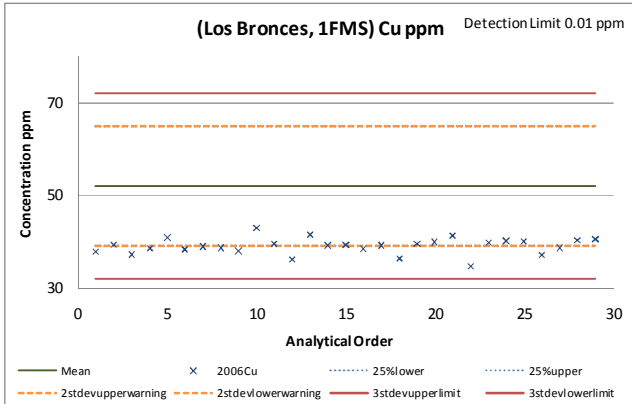
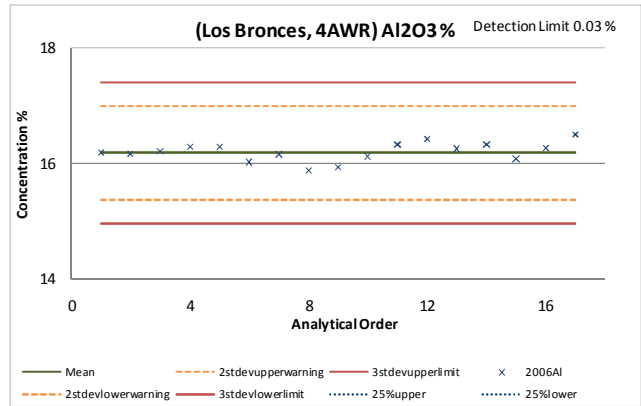
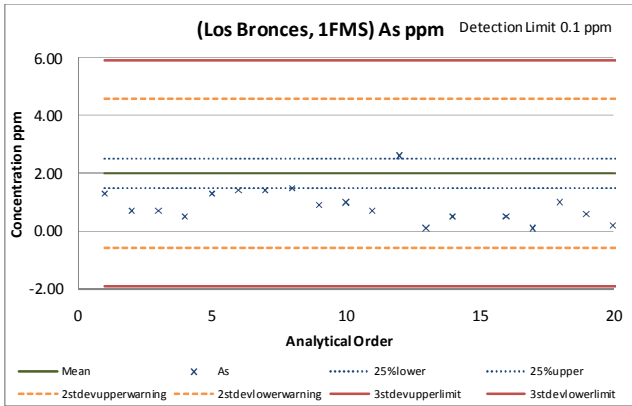


Figure 1: Los Bronces rocks, Standards Graphs.

LH = Olivine Basalt SRM, As, Cu, Fe, Ni. RH = Alkali Altered Andesite SRM, Al, Pb, U, Zn.

Green line represents the reference mean of the SRM of the indicated element, dashed orange lines = ± 2 std dev., dashed red lines = ± 3 std dev., dashed blue lines = $\pm 25\%$ of mean.

(Los Bronces Rocks) Summary of accuracy assessments for the Olivine Basalt SRM
Table 6: Olivine Basalt – AWR
4AWR (1)

Element	Si_%	Al_%	Fe_%	Mg_%	Ca_%	Na_%	K_%	Ti_%	P_%	Mn_%	Cr_%	Ba_ppm
Within 2 SD						x	x		x	x	x	
Within 3 SD				x								
Within ±25%	x	x	x		x			x				x
≤3 outside ±25%												
Outside Limits												
Evaluation												
mean 4AWR data	51.1	14.29	11.27	7.17	8.52	3.08	0.81	1.90	0.30	0.14	0.036	271
mean (olivine basalt) certified	51.7	14.46	11.40	6.84	8.49	3.11	0.84	1.83	0.31	0.14	0.037	285
Bias ¹	-0.013	-0.012	-0.011	0.048	0.004	-0.008	-0.033	0.036	-0.024	0.013	-0.019	-0.050
% Bias ²	-1	-1.2	-1.1	4.83	0.4	-0.83	-3.29	3.6	-2.4	1.3	-1.9	-5.0
mean of data	62.99	15.82	5.75	1.99	3.49	3.25	2.21	0.88	0.21	0.11	0.006	479
detection limit	0.02	0.03	0.04	0.01	0.01	0.01	0.04	0.01	0.01	0.01	0.001	5
10x detection limit	100	100	100	50	60	50	50	100	50	50	100	50000

4AWR (2)

Element	Si_%	Al_%	Fe_%	Mg_%	Ca_%	Na_%	K_%	Ti_%	P_%	Mn_%	Cr_%	Ba_ppm
Within 2 SD											x	
Within 3 SD						x						
Within ±25%	x	x	x									
≤3 outside ±25%				x	x			x	x	x		x
Outside Limits							x					
Evaluation							1 outside > ±25%†					
mean 4AWR data	52.2	14.53	10.81	6.76	8.04	3.21	1.03	1.85	0.29	0.14	0.037	304
mean (olivine basalt) certified	51.7	14.46	11.40	6.84	8.49	3.11	0.84	1.83	0.31	0.14	0.037	285
Bias ¹	0.008	0.005	-0.052	-0.011	-0.053	0.032	0.230	0.008	-0.078	-0.018	-0.005	0.066
% Bias ²	1	0.5	-5.2	-1.13	-5.3	3.24	23.02	0.8	-7.8	-1.8	-0.5	6.6
mean of data	62.99	15.82	5.75	1.99	3.49	3.25	2.21	0.88	0.21	0.11	0.006	479
detection limit	0.02	0.03	0.04	0.01	0.01	0.01	0.04	0.01	0.01	0.01	0.002	5
10x detection limit	100	100	100	50	60	50	50	100	50	50	100	50000

Los Bronces Olivine Basalt 4AWR (1) Standard	
13	Total no. of elements evaluated
12	Total no. of elements meeting QC criterion ^A
5	Elements within 2 std dev of mean
6	Elements within 3 std dev of mean
12	Elements within ±25% of mean
12	Elements with ≤3 points outside ±25% of mean
0	Total no. of elements not meeting QC criterion ^B
0	Elements with ≥4 points outside ±25% of mean
0	Total no. of elements excluded from QC criterion
0	Elements below detection limit
0	Elements too close to detection limit
1	Elements with no certified values for S4 ³
% Elements Meeting Criterion*: $\frac{12}{(12+0)} \times 100$	
100%	
% Elements within ±3 std dev and/or ±25 of mean: 100%	

Los Bronces Olivine Basalt 4AWR (2) Standard	
13	Total no. of elements evaluated
12	Total no. of elements meeting QC criterion ^A
1	Elements within 2 std dev of mean
2	Elements within 3 std dev of mean
5	Elements within ±25% of mean
11	Elements with ≤3 points outside ±25% of mean
1	Total no. of elements not meeting QC criterion ^B
1	Elements with ≥4 points outside ±25% of mean
0	Total no. of elements excluded from QC criterion
0	Elements below detection limit
0	Elements too close to detection limit
1	Elements with no certified values for S4 ³
% Elements Meeting Criterion*: $\frac{12}{(12+1)} \times 100$	
92%	
% Elements within ±3 std dev and/or ±25 of mean: 38%	

Colour Code for Bias	
	>10%
	5 to 10%
	2 to 5%
	-2 to 2%
	-2 to -5%
	-5 to -10%
	<-10%

¹ bias =

$$\frac{(x \text{ data} - x \text{ standard})}{x \text{ standard}}$$
² % bias =

$$\text{bias} * 100$$

³ Sc

³ Sc

Table 7: Olivine Basalt – 1FMS

Element	As_ppm	Co_ppm	Cr_ppm	Cu_ppm	Ni_ppm	Pb_ppm	Sb_ppm	Zn_ppm
Within 2 SD	x						x	
Within 3 SD				x				
Within ±25%								
≤3 outside ±25%					x			
Outside Limits		x	x			x		x
Evaluation		28 points outside ±25%	all points outside ±25%			all points outside ±25%		all points outside ±25%
mean 1FMS data	0.3	29.2	26.3	39.08	111.6	0.84	0.04	67.5
mean (olivine basalt) certified	2.0	44	221	52	141	2.9	0.14	114
Bias ¹	-0.86	-0.34	-0.88	-0.25	-0.21	-0.71	-0.68	-0.41
% Bias ²	-86	-33.5	-88.1	-24.84	-20.8	-71.11	-68.23	-40.8
mean of data	16.6	11.9	23.7	176.12	14.6	34.16	4.34	90.5
detection limit	0.1	0.1	0.5	0.01	0.1	0.01	0.02	0.1
10x detection limit	1.0	1.0	5.00	0.10	1.0	0.10	0.20	1.0

Los Bronces Olivine Basalt 1FMS Standard	
26	Total no. of elements evaluated
4	Total no. of elements meeting QC criterion ^A
2	Elements within 2 std dev of mean
3	Elements within 3 std dev of mean
3	Elements within ±25% of mean
4	Elements with ≤3 points outside ±25% of mean
4	Total no. of elements not meeting QC criterion ^B
4	Elements with ≥4 points outside ±25% of mean
0	Total no. of elements excluded from QC criterion
0	Elements below detection limit
0	Elements too close to detection limit
18	Elements with no certified values for S4 ³
% Elements Meeting Criterion*: $\frac{A}{(A+B)} \times 100$	
	50%
% Elements within ±3 std dev and/or ±25 of mean:	
	38%

Colour Code for Bias	
	>10%
	5 to 10%
	2 to 5%
	-2 to 2%
	-2 to -5%
	-5 to -10%
	<-10%

¹ bias = $\frac{(x_{data} - x_{standard})}{x_{standard}}$
² % bias = bias * 100

³ Mo, Ag, Mn, Au, Cd, Bi, B, Tl, Hg, Se, Te, Ge, In, Re, Be, Li, Pd, Pt

Table 8: Olivine Basalt – 4BWR
4BWR (1)

Element	Nb_ppm	Rb_ppm	Sr_ppm	Th_ppm	U_ppm	Zr_ppm	Y_ppm	La_ppm	Ce_ppm
Within 2 SD	x				x	x			
Within 3 SD		x		x					
Within ±25%			x				x	x	x
≤3 outside ±25%									
Outside Limits									
Evaluation									
mean 4BWR data	21.1	21.12	421.77	2.98	0.78	139.43	24.40	18.10	37.25
mean (olivine basalt) certified	21.0	22.40	403.00	2.85	0.75	141	22.90	17.40	37.60
Bias ¹	0.005	-0.057	0.047	0.047	0.036	-0.011	0.066	0.040	-0.009
% Bias ²	1	-5.7	4.7	4.72	3.6	-1.11	6.55	4.0	-0.9
mean of data	6.76	66.03	503.57	10.99	3.05	197.26	18.59	17.40	39.55
detection limit	0.1	0.5	0.5	0.1	0.1	0.5	0.1	0.5	0.1
10x detection limit	1	5	5	1	1	5	1	5	1

4BWR (2)

Element	Nb_ppm	Rb_ppm	Sr_ppm	Th_ppm	U_ppm	Zr_ppm	Y_ppm	La_ppm	Ce_ppm
Within 2 SD	x			x	x	x		x	
Within 3 SD									
Within ±25%		x	x				x		x
≤3 outside ±25%									
Outside Limits									
Evaluation									
mean 4BWR data	20.3	20.44	422.59	2.79	0.68	136.07	24.56	16.94	37.46
mean (olivine basalt) certified	21.0	22.40	403.00	2.85	0.75	141	22.90	17.40	37.60
Bias ¹	-0.033	-0.087	0.049	-0.021	-0.096	-0.035	0.072	-0.026	-0.004
% Bias ²	-3	-8.7	4.9	-2.14	-9.6	-3.50	7.23	-2.6	-0.4
mean of data	6.76	66.03	503.57	10.99	3.05	197.26	18.59	17.40	39.55
detection limit	0.5	0.5	0.5	0.1	0.1	0.5	0.1	0.5	0.5
10x detection limit	5	5	5	1	1	5	1	5	5

4BWR (3)

Element	Nb_ppm	Rb_ppm	Sr_ppm	Th_ppm	U_ppm	Zr_ppm	Y_ppm	La_ppm	Ce_ppm
Within 2 SD	x	x	x	x	x	x	x	x	x
Within 3 SD									
Within ±25%									
≤3 outside ±25%									
Outside Limits									
Evaluation									
mean 4BWR data	19.6	21.54	402.69	2.77	0.70	131.83	22.31	17.41	37.11
mean (olivine basalt) certified	21.0	22.40	403.00	2.85	0.75	141	22.90	17.40	37.60
Bias ¹	-0.067	-0.038	-0.001	-0.028	-0.067	-0.065	-0.026	0.001	-0.013
% Bias ²	-7	-3.8	-0.1	-2.76	-6.7	-6.50	-2.56	0.1	-1.3
mean of data	6.76	66.03	503.57	10.99	3.05	197.26	18.59	17.40	39.55
detection limit	0.1	0.1	0.5	0.2	0.1	0.1	0.1	0.1	0.1
10x detection limit	1	1	5	2	1	1	1	1	1

Los Bronces Olivine Basalt 4BWR (1) Standard		
9	Total no. of elements evaluated	
9	Total no. of elements meeting QC criterion ^A	
3	Elements within 2 std dev of mean	
5	Elements within 3 std dev of mean	
9	Elements within ±25% of mean	
9	Elements with ≤3 points outside ±25% of mean	
0	Total no. of elements not meeting QC criterion ^B	
0	Elements with ≥4 points outside ±25% of mean	
0	Total no. of elements excluded from QC criterion	
0	Elements below detection limit	
0	Elements too close to detection limit	
19	Elements with no certified values for S4 ³	
% Elements Meeting Criterion*: $\frac{*(A/(A+B)) \times 100}{}$		100%
% Elements within ±3 std dev and/or ±25 of mean:		100%

³ Cs, Ga, Hf, Sn, Ta, V, W, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu

Los Bronces Olivine Basalt 4BWR (3) Standard		
9	Total no. of elements evaluated	
9	Total no. of elements meeting QC criterion ^A	
9	Elements within 2 sd of mean	
9	Elements within 3 sd of mean	
9	Elements within ±25% of mean	
9	Elements with ≤3 points outside ±25% of mean	
0	Total no. of elements not meeting QC criterion ^B	
0	Elements with ≥4 points outside ±25% of mean	
0	Total no. of elements excluded from QC criterion	
0	Elements below detection limit	
0	Elements too close to detection limit	
19	Elements with no certified values for S4 ³	
% Elements Meeting Criterion*: $\frac{*(A/(A+B)) \times 100}{}$		100%
% Elements within ±3 std dev and/or ±25 of mean:		100%

³ Cs, Ga, Hf, Sn, Ta, V, W, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu

Los Bronces Olivine Basalt 4BWR (2) Standard		
9	Total no. of elements evaluated	
9	Total no. of elements meeting QC criterion ^A	
5	Elements within 2 sd of mean	
5	Elements within 3 sd of mean	
9	Elements within ±25% of mean	
9	Elements with ≤3 points outside ±25% of mean	
0	Total no. of elements not meeting QC criterion ^B	
0	Elements with ≥4 points outside ±25% of mean	
0	Total no. of elements excluded from QC criterion	
0	Elements below detection limit	
0	Elements too close to detection limit	
19	Elements with no certified values for S4 ³	
% Elements Meeting Criterion*: $\frac{*(A/(A+B)) \times 100}{}$		100%
% Elements within ±3 std dev and/or ±25 of mean:		100%

³ Cs, Ga, Hf, Sn, Ta, V, W, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu

Colour Code for Bias	
	>10%
	5 to 10%
	2 to 5%
	-2 to 2%
	-2 to -5%
	-5 to -10%
	<-10%

$$^1 \text{ bias} = \frac{(x_{\text{data}} - x_{\text{standard}})}{x_{\text{standard}}}$$

$$^2 \text{ \% bias} = \text{bias} * 100$$

Table 9: Olivine Basalt – 4ALC

Element	TOT/C_%	TOT/S_%
Within 2 SD		
Within 3 SD		
Within ±25%		
≤3 outside ±25%		
Outside Limits	x	
Evaluation	1 outside > ±25%†	too close to detection limit
mean 4ALC data	0.10	
mean (olivine basalt) certified	0.08	
Bias ¹	0.20	
% Bias ²	20	
mean of data	0.1	0.2
detection limit	0.1	0.1
10x detection limit	1.0	1.0

Los Bronces Olivine Basalt 4ALC Standard		
2	Total no. of elements evaluated	
0	Total no. of elements meeting QC criterion ^A	
0	Elements within 2 std dev of mean	
0	Elements within 3 std dev of mean	
0	Elements within ±25% of mean	
0	Elements with ≤3 points outside ±25% of mean	
1	Total no. of elements not meeting QC criterion ^B	
1	Elements with ≥4 points outside ±25% of mean	
1	Total no. of elements excluded from QC criterion	
0	Elements below detection limit	
1	Elements too close to detection limit	
0	Elements with no certified values for S4	
% elements meeting QC criterion*: $\frac{*(A/(A+B)) \times 100}{}$		0%
% Elements within ±3 std dev and/or ±25 of mean:		0%

Colour Code for Bias	
	>10%
	5 to 10%
	2 to 5%
	-2 to 2%
	-2 to -5%
	-5 to -10%
	<-10%

$$^1 \text{ bias} =$$

$$\frac{(x_{\text{data}} - x_{\text{standard}})}{x_{\text{standard}}}$$

$$^2 \text{ \% bias} =$$

$$\text{bias} * 100$$

Table 10: Olivine Basalt – 7TDA

Element	Ni_ppm
Within 2 SD	
Within 3 SD	
Within ±25%	x
≤3 outside ±25%	
Outside Limits	
Evaluation	
mean 7TDA data	143.2
mean (olivine basalt) certified	141.0
Bias ¹	0.02
% Bias ²	2
mean of data	18.3
detection limit	10.0
10x detection limit	100.0

Los Bronces Olivine Basalt 7TDA Standard	
1	Total no. of elements evaluated
1	Total no. of elements meeting QC criterion ^A
0	Elements within 2 std dev of mean
0	Elements within 3 std dev of mean
1	Elements within ±25% of mean
1	Elements with ≤3 points outside ±25% of mean
0	Total no. of elements not meeting QC criterion ^B
0	Elements with ≥4 points outside ±25% of mean
0	Total no. of elements excluded from QC criterion
0	Elements below detection limit
0	Elements too close to detection limit
0	Elements with no certified values for S4
% Elements Meeting Criterion*: $\frac{1}{((A/(A+B)) \times 100)}$	
	100%
% Elements within ±3 std dev and/or ±25 of mean:	
	100%

Colour Code for Bias	
	>10%
	5 to 10%
	2 to 5%
	-2 to 2%
	-2 to -5%
	-5 to -10%
	<-10%

$$^1 \text{ bias} = \frac{(x_{\text{data}} - x_{\text{standard}})}{x_{\text{standard}}}$$

$$^2 \text{ \% bias} = \text{bias} * 100$$

Table 11: Olivine Basalt – 4ALO
4ALO (1)

Element	LOI_%
Within 2 SD	
Within 3 SD	
Within ±25%	
≤3 outside ±25%	x
Outside Limits	
Evaluation	
mean 4ALO data	1.2
mean (olivine basalt) certified	0.6
Bias ¹	0.94
% Bias ²	94
mean of data	2.7
detection limit	unknown
10x detection limit	N/A

Los Bronces Olivine Basalt 4ALO (1) Standard	
1	Total no. of elements evaluated
1	Total no. of elements meeting QC criterion ^A
0	Elements within 2 std dev of mean
0	Elements within 3 std dev of mean
0	Elements within ±25% of mean
1	Elements with ≤3 points outside ±25% of mean
0	Total no. of elements not meeting QC criterion ^B
0	Elements with ≥4 points outside ±25% of mean
0	Total no. of elements excluded from QC criterion
0	Elements below detection limit
0	Elements too close to detection limit
0	Elements with no certified values for S4
% elements meeting QC criterion*: $\frac{1}{((A/(A+B)) \times 100)}$	
	100%
% Elements within ±3 std dev and/or ±25 of mean:	
	0%

Colour Code for Bias	
	>10%
	5 to 10%
	2 to 5%
	-2 to 2%
	-2 to -5%
	-5 to -10%
	<-10%

$$^1 \text{ bias} = \frac{(x_{\text{data}} - x_{\text{standard}})}{x_{\text{standard}}}$$

$$^2 \text{ \% bias} = \text{bias} * 100$$

4ALO (2)

Element	LOI_%
Within 2 SD	
Within 3 SD	
Within ±25%	
≤3 outside ±25%	
Outside Limits	x
Evaluation	6 outside >±25%†
mean 4ALO data	1.4
mean (olivine basalt) certified	0.6
Bias ¹	1.36
% Bias ²	136
mean of data	2.7
detection limit	0.1
10x detection limit	1.0

Los Bronces Olivine Basalt 4ALO (2) Standard	
1	Total no. of elements evaluated
0	Total no. of elements meeting QC criterion ^A
0	Elements within 2 std dev of mean
0	Elements within 3 std dev of mean
0	Elements within ±25% of mean
0	Elements with ≤3 points outside ±25% of mean
1	Total no. of elements not meeting QC criterion ^B
1	Elements with ≥4 points outside ±25% of mean
0	Total no. of elements excluded from QC criterion
0	Elements below detection limit
0	Elements too close to detection limit
0	Elements with no certified values for S4
% Elements Meeting Criterion*: $\frac{1}{((A/(A+B)) \times 100)}$	
	0%
% Elements within ±3 std dev and/or ±25 of mean:	
	0%

(Los Bronces Rocks) Summary of accuracy assessments for the Alkali Altered Andesite SRM
Table 12: Alkali Altered Andesite – AWR
4AWR (1)

Element	Si_%	Al_%	Fe_%	Mg_%	Ca_%	Na_%	K_%	Ti_%	P_%	Mn_%	Ba_ppm
Within 2 SD	x	x	x			x		x		x	x
Within 3 SD					x						
Within ±25%				x			x				
≤3 outside ±25%											
Outside Limits									x		
Evaluation									2 outside > ±25%†		
mean 4AWR data	57.0	16.20	10.83	2.98	0.09	0.27	8.20	0.67	0.04	0.05	1074
mean (altered andesite) certified	57.5	16.18	10.73	2.95	0.10	0.27	8.25	0.68	0.03	0.05	1094
Bias ¹	-0.009	0.001	0.009	0.010	-0.112	-0.015	-0.006	-0.018	0.176	0.000	-0.019
% Bias ²	-1	0.1	0.9	1.00	-11.2	-1.53	-0.61	-1.8	17.6	0.0	-1.9
mean of data	62.99	15.82	5.75	1.99	3.49	3.25	2.21	0.88	0.21	0.11	479
detection limit	0.02	0.03	0.04	0.01	0.01	0.01	0.04	0.01	0.01	0.01	5
10x detection limit	0.2	0.3	0.4	0.1	0.1	0.1	0.4	0.1	0.1	0.1	50

4AWR (2)

Element	Si_%	Al_%	Fe_%	Mg_%	Ca_%	Na_%	K_%	Ti_%	P_%	Mn_%	Ba_ppm
Within 2 SD	x	x				x		x		x	x
Within 3 SD					x						
Within ±25%			x	x			x				
≤3 outside ±25%											
Outside Limits									x		
Evaluation									2 outside > ±25%†		
mean 4AWR data	56.9	16.41	10.95	2.99	0.08	0.27	8.07	0.67	0.03	0.05	1054
mean (altered andesite) certified	57.5	16.18	10.73	2.95	0.10	0.27	8.25	0.68	0.03	0.05	1094
Bias ¹	-0.011	0.014	0.021	0.013	-0.182	-0.010	-0.022	-0.016	-0.076	0.000	-0.037
% Bias ²	-1	1.4	2.1	1.26	-18.2	-1.01	-2.21	-1.6	-7.6	0.0	-3.7
mean of data	60.93	16.41	6.10	2.34	4.14	4.14	2.69	0.78	0.20	0.12	565
detection limit	0.02	0.03	0.04	0.01	0.01	0.01	0.04	0.01	0.01	0.01	5
10x detection limit	0.2	0.3	0.4	0.1	0.1	0.1	0.4	0.1	0.1	0.1	50

Los Bronces Altered Andesite 4AWR (1) Standard	
13	Total no. of elements evaluated
10	Total no. of elements meeting QC criterion ^A
7	Elements within 2 std dev of mean
8	Elements within 3 std dev of mean
10	Elements within ±25% of mean
10	Elements with ≤3 points outside ±25% of mean
1	Total no. of elements not meeting QC criterion ^B
1	Elements with ≥4 points outside ±25% of mean
0	Total no. of elements excluded from QC criterion
0	Elements below detection limit
0	Elements too close to detection limit
2	Elements with no certified values for S4 ³
	% Elements Meeting Criterion*: $\frac{\%}{\%((A/(A+B)) \times 100)}$
	91%
	% Elements within ±3 std dev and/or ±25 of mean: 91%

Los Bronces Altered Andesite 4AWR (2) Standard	
13	Total no. of elements evaluated
10	Total no. of elements meeting QC criterion ^A
6	Elements within 2 std dev of mean
7	Elements within 3 std dev of mean
10	Elements within ±25% of mean
10	Elements with ≤3 points outside ±25% of mean
1	Total no. of elements not meeting QC criterion ^B
1	Elements with ≥4 points outside ±25% of mean
0	Total no. of elements excluded from QC criterion
0	Elements below detection limit
0	Elements too close to detection limit
2	Elements with no certified values for S4 ³
	% Elements Meeting Criterion*: $\frac{\%}{\%((A/(A+B)) \times 100)}$
	91%
	% Elements within ±3 std dev and/or ±25 of mean: 91%

Colour Code for Bias	
	>10%
	5 to 10%
	2 to 5%
	-2 to 2%
	-2 to -5%
	-5 to -10%
	<-10%

¹ bias =

$$\frac{(x_{data} - x_{standard})}{x_{standard}}$$
² % bias =
 bias * 100

³ Cr, Sc

³ Cr, Sc

Table 13: Alkali Altered Andesite – 1FMS

Element	As_ppm	Au_ppb	Bi_ppm	Co_ppm	Cr_ppm	Cu_ppm	Ni_ppm	Pb_ppm	Sb_ppm	Zn_ppm
Within 2 SD			x	x	x		x	x		x
Within 3 SD										
Within ±25%		x								
≤3 outside ±25%						x				
Outside Limits	x								x	
Evaluation	8 outside > ±25%†								all outside > ±25%†	
mean 1FMS data	3.2	20.2	0.10	48.1	29.0	422.48	19.0	1.96	0.66	17.3
mean (altered andesite) certified	6.0	20.0	0.09	44	30	430	19	2.3	1.4	18
Bias ¹	-0.47	0.01	0.08	0.09	-0.03	-0.02	0.00	-0.15	-0.53	-0.04
% Bias ²	-47	0.9	8.15	9.3	-3.4	-1.75	-0.2	-14.87	-52.74	-3.9
mean of data	16.6	2.2	0.40	11.9	23.7	176.12	14.6	34.16	4.34	90.5
detection limit	0.1	0.2	0.02	0.1	0.5	0.01	0.1	0.01	0.02	0.1
10x detection limit	1.0	2.0	0.20	1.0	5.00	0.10	1.0	0.10	0.20	1.0

Los Bronces Altered Andesite 1FMS Standard	
26	Total no. of elements evaluated
8	Total no. of elements meeting QC criterion^A
6	Elements within 2 std dev of mean
6	Elements within 3 std dev of mean
7	Elements within ±25% of mean
8	Elements with ≤3 points outside ±25% of mean
2	Total no. of elements not meeting QC criterion^B
2	Elements with ≥4 points outside ±25% of mean
0	Total no. of elements excluded from QC criterion
0	Elements below detection limit
0	Elements too close to detection limit
16	Elements with no certified values for S4³
% Elements Meeting Criterion*: $\frac{A}{(A+B)} \times 100$	
	80%
% Elements within ±3 std dev and/or ±25 of mean:	
	70%

Colour Code for Bias	
	>10%
	5 to 10%
	2 to 5%
	-2 to 2%
	-2 to -5%
	-5 to -10%
	<-10%

$$^1 \text{ bias} = \frac{(x_{\text{data}} - x_{\text{standard}})}{x_{\text{standard}}}$$

$$^2 \text{ \% bias} = \text{bias} * 100$$

³ Mo, Ag, Mn, Cd, Ti, Tl, Hg, Se, Te, Ge, In, Re, Be, Ii, Pd, Pt

Table 14: Alkali Altered Andesite – 4BWR
4BWR (1)

Element	Nb_ppm	Rb_ppm	Sn_ppm	Sr_ppm	Th_ppm	U_ppm	Zr_ppm	Y_ppm	La_ppm	Ce_ppm	Pr_ppm
Within 2 SD	x		x	x	x	x	x				
Within 3 SD											x
Within ±25%		x						x	x	x	
≤3 outside ±25%											
Outside Limits											
Evaluation											
mean 4BWR data	3.8	193.07	4.73	48.58	4.63	1.21	124.40	9.79	4.11	7.43	0.93
mean (altered andesite) certified	4.0	202.00	5.00	46.00	4.5	1.20	129	9.20	4.00	7.40	0.90
Bias ¹	-0.050	-0.044	-0.055	0.056	0.028	0.008	-0.036	0.064	0.027	0.004	0.034
% Bias ²	-5	-4.4	-5.5	5.6	2.83	0.8	-3.57	6.42	2.7	0.4	3.4
mean of data	6.76	66.03	1.99	503.57	10.99	3.05	197.26	18.59	17.40	39.55	5.13895
detection limit	0.1	0.5	1	0.5	0.1	0.1	0.5	0.1	0.1	0.1	0.02
10x detection limit	1	5	10	5	1	1	5	1	1	1	0.2
Element	Nd_ppm	Sm_ppm	Eu_ppm	Gd_ppm	Tb_ppm	Dy_ppm	Ho_ppm	Er_ppm	Tm_ppm	Yb_ppm	Lu_ppm
Within 2 SD	x		x	x					x	x	
Within 3 SD		x				x					
Within ±25%								x			x
≤3 outside ±25%							x				
Outside Limits					x						
Evaluation					1 outside > ±25%†						
mean 4BWR data	3.89	1.0	0.26	1.23	0.26	1.40	0.31	0.91	0.16	1.04	0.18
mean (altered andesite) certified	3.7	1.0	0.20	1.20	0.22	1.5	0.30	1	0.16	1.10	0.19
Bias ¹	0.052	-0.046	0.286	0.027	0.198	-0.065	0.030	-0.085	-0.011	-0.052	-0.077
% Bias ²	5	-5	28.6	2.7	19.8	-6.55	3.0	-8.55	-1.14	-5.2	-7.7
mean of data	20.71	3.92	0.96	3.31	0.61	2.86	0.58	1.64	0.27	1.73	0.27
detection limit	0.3	0.05	0.02	0.05	0.01	0.05	0.02	0.03	0.01	0.05	0.01
10x detection limit	3	0.5	0.2	0.5	0.1	0.5	0.2	0.3	0.1	0.5	0.1

Los Bronces Altered Andesite 4BWR (1) Standard	
22	Total no. of elements evaluated
21	Total no. of elements meeting QC criterion ^A
11	Elements within 2 std dev of mean
14	Elements within 3 std dev of mean
20	Elements within ±25% of mean
21	Elements with ≤3 points outside ±25% of mean
1	Total no. of elements not meeting QC criterion ^B
1	Elements with ≥4 points outside ±25% of mean
0	Total no. of elements excluded from QC criterion
0	Elements below detection limit
0	Elements too close to detection limit
6	Elements with no certified values for S4 ³
% Elements Meeting Criterion*: $\frac{A}{(A+B)} \times 100$	
	95%
% Elements within ±3 std dev and/or ±25 of mean:	
	91%

Colour Code for Bias	
	>10%
	5 to 10%
	2 to 5%
	-2 to 2%
	-2 to -5%
	-5 to -10%
	<-10%

$$^1 \text{ bias} = \frac{(x_{\text{data}} - x_{\text{standard}})}{x_{\text{standard}}}$$

$$^2 \% \text{ bias} = \text{bias} * 100$$

³ Cs, Ga, Hf, Ta, V, W

4BWR (2)

Element	Nb_ppm	Rb_ppm	Sn_ppm	Sr_ppm	Th_ppm	U_ppm	Zr_ppm	Y_ppm	La_ppm	Ce_ppm	Pr_ppm
Within 2 SD	x	x	x	x	x	x	x		x		x
Within 3 SD										x	
Within ±25%								x			
≤3 outside ±25%											
Outside Limits											
Evaluation											
mean 4BWR data	3.57	189.92	4.44	47.01	4.36	1.08	120.93	9.96	3.80	7.49	0.89
mean (altered andesite) certified	4.00	202.00	5.00	46.00	4.50	1.20	129.00	9.20	4.00	7.40	0.90
Bias ¹	-0.108	-0.060	-0.111	0.022	-0.032	-0.102	-0.063	0.082	-0.050	0.012	-0.014
% Bias ²	-11	-6.0	-11.1	2.2	-3.21	-10.2	-6.25	8.21	-5.0	1.2	-1.4
mean of data	5.81	85.46	1.57	512.59	10.58	3.04	170.22	13.62	17.14	39.57	4.806987
detection limit	0.1	0.5	1	0.5	0.1	0.1	0.5	0.1	0.1	0.1	0.02
10x detection limit	1	5	10	5	1	1	5	1	1	1	0.2
Element	Nd_ppm	Sm_ppm	Eu_ppm	Gd_ppm	Tb_ppm	Dy_ppm	Ho_ppm	Er_ppm	Tm_ppm	Yb_ppm	Lu_ppm
Within 2 SD	x		x	x		x		x	x	x	x
Within 3 SD		x			x						
Within ±25%							x				
≤3 outside ±25%											
Outside Limits											
Evaluation											
mean 4BWR data	3.68	1.0	0.24	1.21	0.25	1.42	0.29	0.92	0.15	1.02	0.17
mean (altered andesite) certified	3.7	1.0	0.20	1.20	0.22	1.5	0.30	1	0.16	1.10	0.19
Bias ¹	-0.006	-0.047	0.206	0.005	0.157	-0.055	-0.019	-0.077	-0.049	-0.074	-0.117
% Bias ²	-1	-5	20.6	0.5	15.7	-5.48	-1.9	-7.67	-4.86	-7.4	-11.7
mean of data	19.05	3.48	0.79	2.66	0.45	2.19	0.40	1.18	0.18	1.18	0.18
detection limit	0.3	0.05	0.02	0.05	0.01	0.05	0.02	0.03	0.01	0.05	0.01
10x detection limit	3	0.5	0.2	0.5	0.1	0.5	0.2	0.3	0.1	0.5	0.1

Los Bronces Altered Andesite 4BWR (2) Standard

22	Total no. of elements evaluated	
22	Total no. of elements meeting QC criterion ^A	
17	Elements within 2 std dev of mean	
20	Elements within 3 std dev of mean	
22	Elements within ±25% of mean	
22	Elements with ≤3 points outside ±25% of mean	
0	Total no. of elements not meeting QC criterion ^B	
0	Elements with ≥4 points outside ±25% of mean	
0	Total no. of elements excluded from QC criterion	
0	Elements below detection limit	
0	Elements too close to detection limit	
6	Elements with no certified values for S4 ³	
% Elements Meeting Criterion*: <small>*((A/(A+B))x100)</small>		100%
% Elements within ±3 std dev and/or ±25 of mean:		100%

Colour Code for Bias

	>10%
	5 to 10%
	2 to 5%
	-2 to 2%
	-2 to -5%
	-5 to -10%
	<-10%

¹ bias =
$$\frac{(x_{data} - x_{standard})}{x_{standard}}$$

² % bias =
$$bias * 100$$

³ Cs, Ga, Hf, Ta, V, W

4BWR (3)

Element	Nb_ppm	Rb_ppm	Sn_ppm	Sr_ppm	Th_ppm	U_ppm	Zr_ppm	Y_ppm	La_ppm	Ce_ppm	Pr_ppm
Within 2 SD	x	x	x	x	x	x	x		x		x
Within 3 SD											
Within ±25%								x		x	
≤3 outside ±25%											
Outside Limits											
Evaluation											
mean 4BWR data	3.46	192.42	4.56	45.29	4.23	1.12	116.36	8.80	3.73	7.27	0.88
mean (altered andesite) certified	4.00	202.00	5.00	46.00	4.50	1.20	129.00	9.20	4.00	7.40	0.90
Bias ¹	-0.136	-0.047	-0.089	-0.015	-0.059	-0.065	-0.098	-0.043	-0.067	-0.018	-0.027
% Bias ²	-14	-4.7	-8.9	-1.5	-5.93	-6.5	-9.80	-4.35	-6.7	-1.8	-2.7
mean of data	6.44	63.33	1.49	430.61	7.64	2.26	171.34	23.51	19.01	44.23	5.595833
detection limit	0.1	0.1	1	0.5	0.2	0.1	0.1	0.1	0.1	0.1	0.02
10x detection limit	1	1	10	5	2	1	1	1	1	1	0.2
Element	Nd_ppm	Sm_ppm	Eu_ppm	Gd_ppm	Tb_ppm	Dy_ppm	Ho_ppm	Er_ppm	Tm_ppm	Yb_ppm	Lu_ppm
Within 2 SD	x	x	x	x	x	x		x	x	x	x
Within 3 SD											
Within ±25%							x				
≤3 outside ±25%											
Outside Limits											
Evaluation											
mean 4BWR data	3.59	1.0	0.26	1.20	0.23	1.41	0.31	0.95	0.15	1.02	0.17
mean (altered andesite) certified	3.7	1.0	0.20	1.20	0.22	1.5	0.30	1	0.16	1.10	0.19
Bias ¹	-0.030	-0.029	0.322	-0.004	0.056	-0.060	0.022	-0.048	-0.049	-0.072	-0.117
% Bias ²	-3	-3	32.2	-0.4	5.6	-6.00	2.2	-4.78	-4.86	-7.2	-11.7
mean of data	23.76	4.97	1.26	4.51	0.74	4.10	0.82	2.41	0.36	2.32	0.35
detection limit	0.3	0.05	0.02	0.05	0.01	0.05	0.02	0.03	0.01	0.05	0.01
10x detection limit	3	0.5	0.2	0.5	0.1	0.5	0.2	0.3	0.1	0.5	0.1

Los Bronces Altered Andesite 4BWR (3) Standard

22	Total no. of elements evaluated	
22	Total no. of elements meeting QC criterion^A	
19	Elements within 2 std dev of mean	
19	Elements within 3 std dev of mean	
22	Elements within ±25% of mean	
22	Elements with ≤3 points outside ±25% of mean	
0	Total no. of elements not meeting QC criterion^B	
0	Elements with ≥4 points outside ±25% of mean	
0	Total no. of elements excluded from QC criterion	
0	Elements below detection limit	
0	Elements too close to detection limit	
6	Elements with no certified values for S4³	
% Elements Meeting Criterion*: <small>*((A/(A+B))x100)</small>		100%
% Elements within ±3 std dev and/or ±25 of mean:		100%

Colour Code for Bias

	>10%
	5 to 10%
	2 to 5%
	-2 to -5%
	-5 to -10%
	<-10%

¹ bias =

$$\frac{(x_{data} - x_{standard})}{x_{standard}}$$

² % bias =

$$bias * 100$$

³ Cs, Ga, Hf, Ta, V, W

Table 15: Alkali Altered Andesite – 7TDA

Element	Ni_ppm	Los Bronces Altered Andesite 7TDA Standard		Colour Code for Bias
Within 2 SD		1	Total no. of elements evaluated	>10%
Within 3 SD		0	Total no. of elements meeting QC criterion ^A	5 to 10%
Within ±25%		0	Elements within 2 std dev of mean	2 to 5%
≤3 outside ±25%		0	Elements within 3 std dev of mean	-2 to 2%
Outside Limits	x	0	Elements within ±25% of mean	-2 to -5%
Evaluation	4 points >±25%†	0	Elements with ≤3 points outside ±25% of mean	5 to -10%
mean 7TDA data	18.5	1	Total no. of elements not meeting QC criterion ^B	<-10%
mean (altered andesite) certified	19	0	Elements with ≥4 points outside ±25% of mean	
Bias ¹	-0.02	0	Total no. of elements excluded from QC criterion	
% Bias ²	-2.46	0	Elements below detection limit	
mean of data	18.3	0	Elements too close to detection limit	
detection limit	10.0	0	Elements with no certified values for S4	
10x detection limit	100.0	% Elements Meeting Criterion*: *((A/(A+B))x100)		
		% Elements within ±3 std dev and/or ±25 of mean:		

Colour Code for Bias	Bias Range
Red	>10%
Orange	5 to 10%
Yellow	2 to 5%
Light Green	-2 to 2%
Green	-2 to -5%
Light Blue	5 to -10%
Dark Blue	<-10%

¹ bias =

$$\frac{(x_{data} - x_{standard})}{x_{standard}}$$
² % bias =

$$bias * 100$$

Table 16: Alkali Altered Andesite – 4ALO
4ALO (1)

Element	LOI_%
Within 2 SD	
Within 3 SD	
Within ±25%	
≤3 outside ±25%	x
Outside Limits	
Evaluation	
mean 4ALO data	3.4
mean (altered andesite) certified	2.9
Bias ¹	0.19
% Bias ²	19
mean of data	2.7
detection limit	unknown
10x detection limit	N/A

Los Bronces Altered Andesite 4ALO (1) Standard	
1	Total no. of elements evaluated
1	Total no. of elements meeting QC criterion ^A
0	Elements within 2 std dev of mean
0	Elements within 3 std dev of mean
0	Elements within ±25% of mean
1	Elements with ≤3 points outside ±25% of mean
0	Total no. of elements not meeting QC criterion ^B
0	Elements with ≥4 points outside ±25% of mean
0	Total no. of elements excluded from QC criterion
0	Elements below detection limit
0	Elements too close to detection limit
0	Elements with no certified values for S4
% Elements Meeting Criterion*: *((A/(A+B))x100)	
100%	
% Elements within ±3 std dev and/or ±25 of mean:	
0%	

Colour Code for Bias	Bias Range
Red	>10%
Orange	5 to 10%
Yellow	2 to 5%
Light Green	-2 to 2%
Green	-2 to -5%
Light Blue	-5 to -10%
Dark Blue	<-10%

¹ bias =

$$\frac{(x_{data} - x_{standard})}{x_{standard}}$$
² % bias =

$$bias * 100$$

4ALO (2)

Element	LOI_%
Within 2 SD	
Within 3 SD	
Within ±25%	
≤3 outside ±25%	x
Outside Limits	
Evaluation	
mean 4ALO data	3.3
mean (altered andesite) certified	2.9
Bias ¹	0.15
% Bias ²	15
mean of data	2.6
detection limit	0.1
10x detection limit	1.0

Los Bronces Altered Andesite 4ALO (2) Standard	
1	Total no. of elements evaluated
1	Total no. of elements meeting QC criterion ^A
0	Elements within 2 std dev of mean
0	Elements within 3 std dev of mean
0	Elements within ±25% of mean
1	Elements with ≤3 points outside ±25% of mean
0	Total no. of elements not meeting QC criterion ^B
0	Elements with ≥4 points outside ±25% of mean
0	Total no. of elements excluded from QC criterion
0	Elements below detection limit
0	Elements too close to detection limit
0	Elements with no certified values for S4
% Elements Meeting Criterion*: *((A/(A+B))x100)	
100%	
% Elements within ±3 std dev and/or ±25 of mean:	
0%	

Colour Code for Bias	Bias Range
Red	>10%
Orange	5 to 10%
Yellow	2 to 5%
Light Green	-2 to 2%
Green	-2 to -5%
Light Blue	-5 to -10%
Dark Blue	<-10%

¹ bias =

$$\frac{(x_{data} - x_{standard})}{x_{standard}}$$
² % bias =

$$bias * 100$$

Table 17: Alkali Altered Andesite – G3B-MS

Element	Au_ppb
Within 2 SD	
Within 3 SD	
Within ±25%	
≤3 outside ±25%	x
Outside Limits	
Evaluation	
mean G3B-MS data	18.4
mean (altered andesite) certified	20
Bias ¹	-0.08
% Bias ²	-7.92
mean of data	3.2
detection limit	1.0
10x detection limit	10.0

Los Bronces Altered Andesite G3B-MS Standard	
3	Total no. of elements evaluated
1	Total no. of elements meeting QC criterion^A
0	Elements within 2 sd of mean
0	Elements within 3 sd of mean
0	Elements within ±25% of mean
1	Elements with ≤3 points outside ±25% of mean
0	Total no. of elements not meeting QC criterion^B
0	Elements with ≥4 points outside ±25% of mean
0	Total no. of elements excluded from QC criterion
0	Elements below detection limit
0	Elements too close to detection limit
2	Elements with no certified values for S4³
% Elements Meeting Criterion*:	
*((A/(A+B))x100)	
100%	
% Elements within ±3 std dev and/or ±25% of mean:	
0%	

Colour Code for Bias	
	>10%
	5 to 10%
	2 to 5%
	-2 to 2%
	-2 to -5%
	-5 to -10%
	<-10%

¹ bias =

$$\frac{(\bar{x}_{data} - \bar{x}_{standard})}{\bar{x}_{standard}}$$
² % bias =

$$\text{bias} * 100$$

Field Duplicates

During the sampling campaigns, field duplicates were collected to determine the sampling variation (Table 1).

In order to evaluate the precision of the data collected, the percentage relative difference between duplicates was calculated for each analytical method.

The duplicate results are presented as graphs for each chemical element, comparing the percentage relative difference plotted against the original-duplicate mean (1).

$$y\text{-axis: } 100 * \frac{\text{Original} - \text{Duplicate}}{\frac{1}{2}(\text{Original} + \text{Duplicate})} \quad (1)$$

$$x\text{-axis: } \frac{1}{2}(\text{Original} + \text{Duplicate})$$

Two pass-fail criteria were applied to each element;

- 1) An element passed where 90% of values fell within ±25% of the percentage relative difference
- 2) The entire dataset passed if the average percentage relative difference of all analytes was <±25%*

A black solid line which represents ten times the detection limit is plotted parallel to Y axis (Figure 2) or otherwise indicated. Samples less than 10 times the detection limit and elements where more than 50% of samples were less than 10 times the detection limit were excluded from the evaluation.

*Elements with sample concentrations close to detection limits show increased variability resulting from difficulties maintaining accuracy of measurements at low concentrations. The second pass-fail criterion accounts for this by considering the overall average percentage relative difference per element; this reflects the overall behaviour of the dataset and so minimises the variability caused by samples close to the detection limits.

Table 4: Summary of QA/QC reproducibility results for duplicates, grouped according to analytical method

Analytical Method	Percentage of elements meeting first QC criterion	Percentage of elements meeting second QC criterion
	(1) % duplicates with $\geq 90\%$ samples within $\pm 25\%$ of percentage relative difference:	(2) Average of average percentage relative difference:
4AWR	45%	10%
4BWR	17%	14%
4ALO	0%	15%
1FMS	0%	25%
7TDA	N/A	N/A
4ALC	N/A	N/A
G3B-MS	N/A	N/A

(1) Percentage of duplicates with $\geq 90\%$ of samples within $\pm 25\%$ of percentage relative difference (meeting first QC criterion)

For all analytical methods used to analyse the Los Bronces rock samples, the percentage of duplicates with $\geq 90\%$ samples falling within $\pm 25\%$ of relative difference was low (Figure 2). 4AWR had 45% of duplicates with $\geq 90\%$ samples within $\pm 25\%$ of the percentage relative difference whilst 4BWR had 17% (Table 4). The remaining analytical methods either had less than 90% of duplicates which lay within these parameters, or had samples for which results were $< 10x$ the detection limit and therefore excluded from analysis.

This poor performance is thought to reflect the inherent heterogeneity of rock samples and the high variability of the sample media. The chemistry of rocks may vary significantly over mm distance as a result of the changing mineralogy and varied states (e.g. oxidised, reduced) in which elements may be present. However, the average percentage of duplicates within $\pm 25\%$ of percentage relative difference across all datasets was 78%. Although this is lower than the 90% criteria, it demonstrates consistency across the dataset and reflects a level of reproducibility acceptable for use.

To allow for the intrinsic heterogeneity of rock samples an additional pass-fail criterion was established. An element passed if ≥ 3 analysed standard samples for each element were outside $\pm 25\%$ of the mean for that standard.

(2) Average of average percentage relative difference (meeting second QC criterion)

All applicable datasets (4AWR, 4BWR, 4ALO and 1FMS analytical methods) met the second QC criterion as they all showed an average percentage relative difference less than $\pm 25\%$ (Table 4). The datasets for 7TDA, 4ALC and G3B-MS methods contained elements which were below $10x$ detection limit and therefore were excluded from QA/QC evaluation.

Overall, although the performance of the datasets under the first criterion was low, the performance against the second criterion suggests that this reflects the intrinsic heterogeneity of the rock samples.

Overall, the data is acceptable for use.

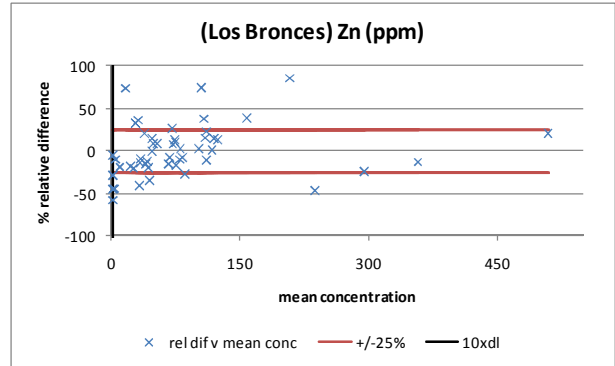
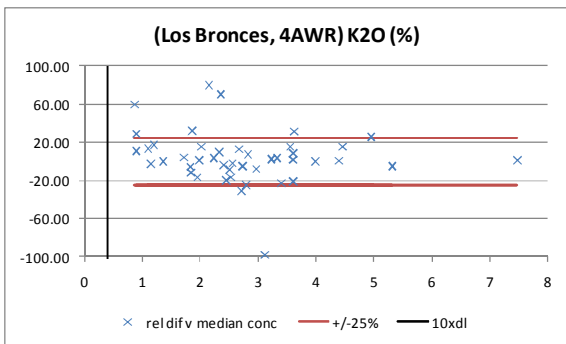
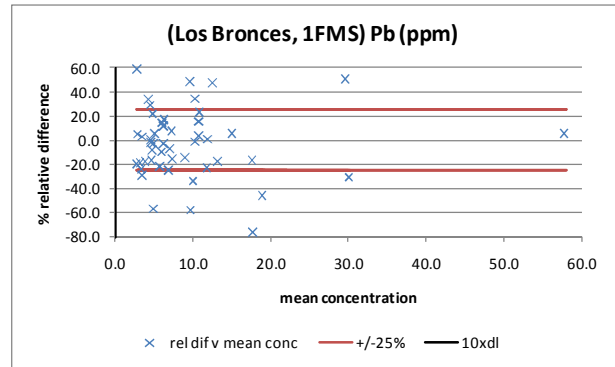
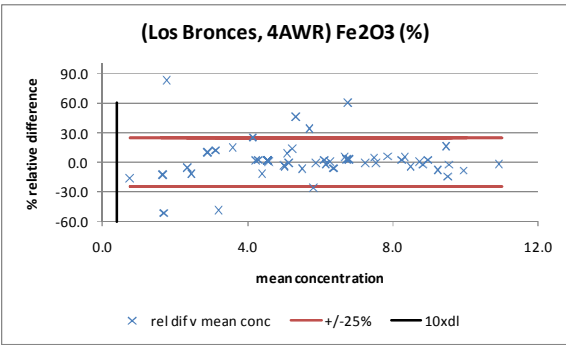
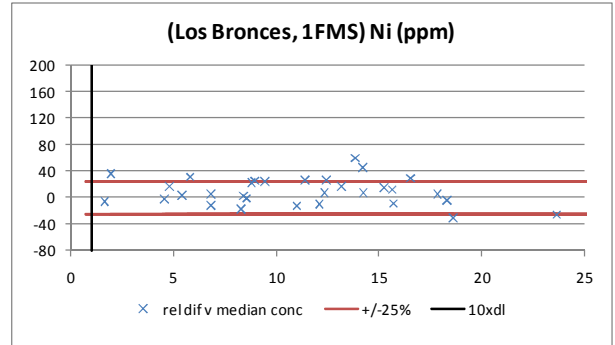
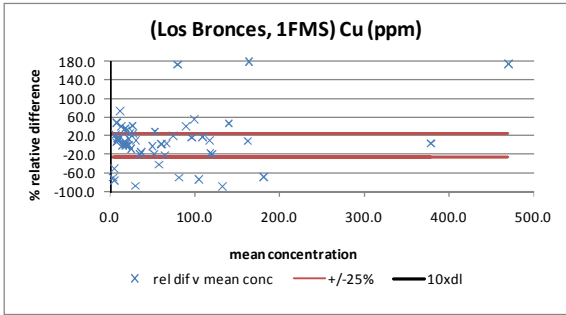
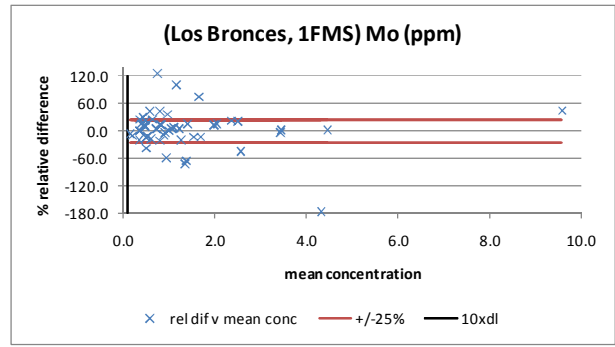
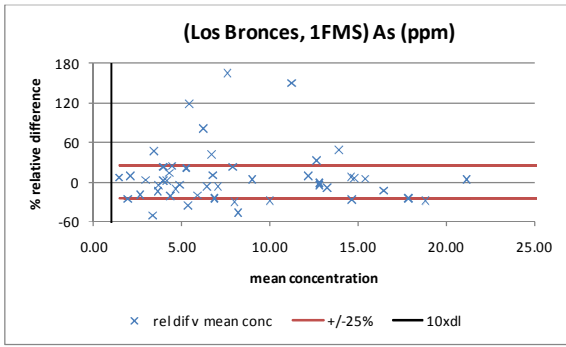


Figure 2: Los Bronces Rocks – Duplicates Graphs. As, Cu, Fe, K, Mo, Ni, Pb, Zn. Horizontal red lines represent $\pm 25\%$ error margins. Vertical black lines represent ten times the detection limit for each element.

(Los Bronces Rocks) Reproducibility assessment for field duplicates
Table 18: 4AWR

Element	SiO2 (%)	Al2O3 (%)	Fe2O3 (%)	MgO (%)	CaO (%)	Na2O (%)	K2O (%)	TiO2 (%)	P2O5 (%)	MnO (%)	Cr2O3 (%)	Ba (ppm)	Sc (ppm)
10x det. limit	0.2	0.3	0.4	0.1	0.1	0.1	0.4	0.1	0.1	0.1	0.02	50	10
no samples outside ±25%	0	1	7	6	8	5	9	3	6			10	2
% within error	100	98	84	87	83	90	80	94	87			80	94
≥90% data within ±25%	x	x				x		x					x
samples <10x det. limit										x	x		
<90% within ±25%			x	x	x		x		x			x	
Average % relative difference	3	4	12	12	15	12	18	8	12	N/A	N/A	17	7

Los Bronces 4AWR Duplicates - Summary	
13	Total no. of elements evaluated
5	Total no. of elements meeting first QC criterion ^A
5	≥90% duplicates within ±25% of %relative difference
6	Total no. of elements not meeting first QC criterion ^B
6	<90% duplicates within ±25% of %relative difference
2	Total no. of elements excluded from first QC criterion
2	>50% of samples below 10x detection limit
(1)	% duplicates with ≥90% samples within ±25% of relative difference $((A/(A+B)) \times 100)$
	45%
(2)	Average of average % relative difference:
	11%

Table 19: 4BWR

Element	Cs (ppm)	Ga (ppm)	Hf (ppm)	Nb (ppm)	Rb (ppm)	Sn (ppm)	Sr (ppm)	Ta (ppm)	Th (ppm)	U (ppm)	V (ppm)	W (ppm)	Zr (ppm)
10x det. limit	1	5	5	5	5	10	5	1	2	1	80	5	5
no samples outside ±25%	6	2	1	6	9		7		10	10	9		4
% within error	83	96	96	83	80		86		80	77	80		92
≥90% data within ±25%		x	x										x
samples <10x det. limit						x		x				x	
<90% within ±25%	x			x	x		x		x	x	x		
Average % relative difference	23	8	10	18	17	N/A	13	N/A	19	19	12	N/A	11
Element	Y (ppm)	La (ppm)	Ce (ppm)	Pr (ppm)	Nd (ppm)	Sm (ppm)	Eu (ppm)	Gd (ppm)	Tb (ppm)	Dy (ppm)	Ho (ppm)	Er (ppm)	Tm (ppm)
10x det. limit	1	5	5	0.2	4	1	0.5	0.5	0.1	0.5	0.5	0.5	0.5
no samples outside ±25%	9	5	7	7	7	9	6	9	10	9			9
% within error	82	90	86	86	86	82	87	82	80	82			82
≥90% data within ±25%		x											
samples <10x det. limit											x		x
<90% within ±25%	x		x	x	x	x	x	x	x	x		x	
Average % relative difference	15	10	11	12	12	13	11	13	14	14	9	15	N/A
Element	Yb (ppm)	Lu (ppm)											
10x det. limit	0.5	0.1											
no samples outside ±25%	11	4											
% within error	78	89											
≥90% data within ±25%													
samples <10x det. limit													
<90% within ±25%	x	x											
Average % relative difference	15	14											

Los Bronces 4BWR Duplicates - Summary

28	Total no. of elements evaluated
4	Total no. of elements meeting first QC criterion ^A
4	≥90% duplicates within ±25% of %relative difference
19	Total no. of elements not meeting first QC criterion ^B
19	<90% duplicates within ±25% of %relative difference
5	Total no. of elements excluded from first QC criterion
5	>50% of samples below 10x detection limit
(1)	% duplicates with ≥90% samples within ±25% of relative difference $((A/(A+B)) \times 100)$
	17%
(2)	Average of average % relative difference:
	14%

Table 20: 1FMS

Element	Mo (ppm)	Cu (ppm)	Pb (ppm)	Zn (ppm)	Ag (ppb)	Ni (ppm)	Co (ppm)	Mn (ppm)	As (ppm)	Au (ppb)	Cd (ppm)	Sb (ppm)	Bi (ppm)
10x det. limit	0.1	0.1	0.1	1	20	1	1	10	1	2	0.1	0.2	0.2
no samples outside ±25%	15	22	17	17	24	5	14	15	18			10	
% within error	70	57	67	67	47	88	69	70	65			70	
≥90% data within ±25%													
samples <10x det. limit										x	x		x
<90% within ±25%	x	x	x	x	x	x	x	x	x			x	
Average % relative difference	27	38	25	23	38	19	20	20	29	N/A	N/A	23	N/A
Element	Cr (ppm)	B (ppm)	Ti (ppm)	Hg (ppb)	Se (ppm)	Te (ppm)	Ge (ppm)	In (ppm)	Re (ppb)	Be (ppm)	Li (ppm)	Pd (ppb)	Pt (ppb)
10x det. limit	5	10	0.2	50	1	0.2	1	0.2	10	1	1	100	20
no samples outside ±25%	8											7	
% within error	79											84	
≥90% data within ±25%													
samples <10x det. limit		x	x	x	x	x	x	x	x	x		x	x
<90% within ±25%	x										x		
Average % relative difference	20	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	19	N/A	N/A

Los Bronces 1FMS Duplicates - Summary	
26	Total no. of elements evaluated
0	Total no. of elements meeting first QC criterion ^A
0	≥90% duplicates within ±25% of %relative difference
12	Total no. of elements not meeting first QC criterion ^B
12	<90% duplicates within ±25% of %relative difference
14	Total no. of elements excluded from QC criterion
14	>50% of samples below 10x detection limit
(1) % duplicates with ≥90% samples within ±25% of relative difference $((A/(A+B)) \times 100)$	0%
(2) Average of average % relative difference:	25%

Table 21: 4ALO

Element	LOI (%)
10x det. limit	1
no samples outside ±25%	7
% within error	79
≥90% data within ±25%	
samples <10x det. limit	
<90% within ±25%	x
Average % relative difference	15

Los Bronces LOI Duplicates - Summary	
1	Total no. of elements evaluated
0	Total no. of elements meeting first QC criterion ^A
0	≥90% duplicates within ±25% of %relative difference
1	Total no. of elements not meeting first QC criterion ^B
1	<90% duplicates within ±25% of %relative difference
0	Total no. of elements excluded from first QC criterion
0	>50% of samples below 10x detection limit
(1) % duplicates with ≥90% samples within ±25% of relative difference $((A/(A+B)) \times 100)$	0%
(2) Average of average % relative difference:	15%

Table 22: 7TDA

Element	Ni (ppm)
10x detection limit	100
no samples outside ±25%	
% within error	
≥90% data within ±25%	
samples <10x det. limit	x
<90% within ±25%	
Average % relative difference	N/A

Los Bronces 7TDA Duplicates - Summary	
1	Total no. of elements evaluated
0	Total no. of elements meeting first QC criterion ^A
0	≥90% duplicates within ±25% of %relative difference
0	Total no. of elements not meeting first QC criterion ^B
0	<90% duplicates within ±25% of %relative difference
1	Total no. of elements excluded from first QC criterion
1	>50% of samples below 10x detection limit
(1) % duplicates with ≥90% samples within ±25% of relative difference $((A/(A+B)) \times 100)$	N/A
(2) Average of average % relative difference:	N/A

Table 23: G3B-MS

Element	Au (ppb)	Pt (ppb)	Pd (ppb)
10x det. limit	10	1	5
no samples outside ±25%			
% within error			
≥90% data within ±25%			
samples <10x det. limit	x	x	x
<90% within ±25%			
Average % relative difference			

Los Bronces G3B-MS Duplicates - Summary	
3	Total no. of elements evaluated
0	Total no. of elements meeting first QC criterion ^A
0	≥90% duplicates within ±25% of %relative difference
0	Total no. of elements not meeting first QC criterion ^B
0	<90% duplicates within ±25% of %relative difference
3	Total no. of elements excluded from first QC criterion
3	>50% of samples below 10x detection limit
(1) % duplicates with ≥90% samples within ±25% of relative difference $((A/(A+B)) \times 100)$	N/A
(2) Average of average % relative difference:	N/A

Table 24: 4ALC

Element	TOT/C (%)	TOT/S (%)
10x det. limit	0.1	0.1
no samples outside ±25%		
% within error		
≥90% data within ±25%		
samples <10x det. limit	x	x
<90% within ±25%		
Average % relative difference	N/A	N/A

Los Bronces 4ALC Duplicates - Summary	
2	Total no. of elements evaluated
0	Total no. of elements meeting first QC criterion ^A
0	≥90% duplicates within ±25% of %relative difference
0	Total no. of elements not meeting first QC criterion ^B
0	<90% duplicates within ±25% of %relative difference
2	Total no. of elements excluded from first QC criterion
2	>50% of samples below 10x detection limit
(1) % duplicates with ≥90% samples within ±25% of relative difference $((A/(A+B)) \times 100)$	N/A
(2) Average of average % relative difference:	N/A

QUALITY ASSURANCE/ QUALITY CONTROL OF LITHOGEOCHEMICAL DATA

PROJECT GC51: GEOCHEMICAL BASELINES – COLLAHUASI

**Aisha Gloudon
(PhD student)**

October 2011

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Centre for Environmental Policy

Executive Summary

Rock samples were collected from the Collahuasi region in two campaigns. 1054 samples were collected in 2003-04 and 403 samples in 2006-07 (**Error! Reference source not found.**).

Table 1: The number of samples analysed from Collahuasi region

Campaign	Total Samples	Samples	Field Duplicates	Standards
Collahuasi 2003-04	1054	994	41 (4%)	26 (3%)
Collahuasi 2006-07	403	367	18 (5%)	18 (5%)

Seven analytical techniques, undertaken by Acme Analytical Laboratories (Vancouver) Ltd were used to provide a comprehensive suite of element analytes for the samples as summarised in (Table 2).

Table 2: A summary of analytical techniques used to provide elemental analytes data discussed within this report (undertaken by Acme Analytical Laboratories (Vancouver) Ltd. www.acmelab.com)

Code	Full Name of Analysis (Acme Laboratory)	Technique Used	Datasets
4AWR	Group 4A Whole Rock by ICP	Sample analysed by ICP-emission spectrometry following a Lithium metaborate/tetraborate fusion and dilute nitric acid digestion	Both
4BWR	Group 4B Total Trace Elements by ICP - MS	Rare earth and refractory elements are determined by ICP mass spectrometry following a Lithium metaborate/tetraborate fusion and nitric acid digestion of sample. In addition, a separate split is digested in Aqua Regia and analysed by ICP mass spectrometry to report precious and base metals e.g. Au, Ag, Cd	Both
1FMS	Group 1F-MS Ultratrace by Mass Spec	ICP Mass Spec analysis of a sample after Aqua Regia digestion for low to ultra low determination on soils, sediments and lean rocks	Both
4ALO	Group 4A Whole Rock by ICP (Loss of Ignition)	Weight difference after ignition at 1000 ^o c	Both
4ALC	Group 4A Whole Rock by ICP (LECO)	Total Carbon and Sulphur analysis by LECO	Both
G3B-MS	Group 3B & 3B-MS	A lead-collection fire-assay fusion for total sample decomposition, digestion of the Ag dore bead and ICP-MS analysis.	Both
4BTD	Group 4B Total Trace Elements by ICP - MS	Rare earth and refractory elements are determined by ICP mass spectrometry following four acid digest (HCl-HF-HClO ₄ -HNO ₃)	2003-04 only
7TDA	Group 7 ICP & ICP-MS	Percentage level concentrations as determined by ICP emission spectrometry	2006-07 only

The QA/QC assessment of the rock data shows that the dataset is of high quality.

Standards

The accuracy of the data was assessed by analysing three standards; 2003-04 data was analysed using the OREAS 44P certified reference material (CRM) standard whilst 2006-07 data was analysed using Altered Andesite Whole Rock and Alkali Olivine Basalt (OREAS 24P) secondary reference material (SRM). The accuracy for each analytical method was assessed.

A pass-fail criterion was established whereby an element passed if "3 analysed standard samples for each element outside $\pm 25\%$ of the mean for that standard.

The QA/QC result for standards analysed using each analytical method are summarised in Table 3. For 2003-04 data only the analytical method 4AWR was subject to QA/QC evaluation - this was to verify the findings of previous quality control assessment on this data by Christian Ihlenfeld. For 2006-07 data there was no QA/QC performed for Olivine Basalt standards analysed using G3B-MS (Au, Pt, Pd) as no certified values are available for this method. Similarly, there was no QA/QC performed for the Alkali Altered Andesite standards for carbon and sulphur analysed using 4ALC as there no certified values available. The 4BTD method was only used during the analysis of the 2003-04 data.

Table 3: Summary of QA/QC accuracy results for 2003-04 data, OREAS 44P standard and 2006-07 data, Alkali Altered Andesite and Olivine Basalt standards, grouped according to analytical method

Analytical Method	Percentage of elements meeting QC criterion		
	OREAS 44P (2003-04)	Olivine Basalt (2006-07)	Alkali Altered Andesite (2006-07)
4AWR	100%	100%	92%
4BWR	n/a	100%	100%
1FMS	n/a	50%	80%
4ALO	n/a	0%	100%
4ALC	n/a	100%	n/a
G3B-MS	n/a	n/a	100%
4BTD	n/a	n/a	n/a
7TDA	n/a	100%	100%

Overall, the QA/QC result for standards suggests that the majority of the analytical methods used produce highly accurate data. However, a less satisfactory result was produced for 1FMS and 4ALO methods used on the 2006-07 data than for other analytical methods evaluated, particularly using the Olivine Basalt standard.

The analysis of the Olivine Basalt standard using 1FMS method showed a negative bias across the data analysed. This bias meant that cobalt, chromium, lead and zinc lay outside the QA/QC parameters. However, all cases including those which lay outside the QA/QC parameters, showed a high standard of reproducibility. Additionally, this bias was not reflected in the analysis of the Alkali Altered Andesite data using the same 1FMS method. The same was seen with the 4ALO method, with oxygen performing well using the Alkali Altered Andesite data. Therefore, it is likely that the variability seen with the Olivine Basalt was associated with the standard used rather than the analytical method and so, the data produced using the 1FMS and 4ALO method can be considered as of acceptable quality for use overall.

Field Duplicates

Data were evaluated for precision by comparing duplicates against two pass-fail criteria:

- 1) An element passed if 90% of samples were within $\pm 25\%$ of the percentage relative difference
- 2) The entire dataset passed if the average percentage relative difference of all analytes was $< \pm 25\%$

Table 4: Summary of QA/QC reproducibility results for duplicates, grouped according to dataset and analytical method

Analytical Method	Percentage of elements meeting first QC Criterion		Percentage of elements meeting second Criterion	
	(1) % duplicates with $\geq 90\%$ samples within $\pm 25\%$ of percentage relative difference		(2) Average of average percentage relative difference	
	2003-04	2006-07	2003-04	2006-07
4AWR	100%	46%	2%	10%
4BWR	-	50%	-	11%
1FMS	-	0%	-	32%
7TDA	-	below 10x DL	-	below 10x DL
4ALO	-	below 10x DL	-	below 10x DL
4ALC	-	below 10x DL	-	below 10x DL
G3B-MS	-	below 10x DL	-	below 10x DL

For all analytical methods used to analyse the Collahuasi 2003-04 rock samples, the percentage of duplicates with $\geq 90\%$ samples falling within $\pm 25\%$ of relative difference was 100% (Table 4). For the analytical methods used to analyse the Collahuasi 2006-07 rock samples, the percentage of duplicates with $\geq 90\%$ for 4AWR, 4BWR and 1FMS methods was $\geq 50\%$ (Figure 3). This is low, but is thought to reflect the inherent heterogeneity of rock samples and the high variability of the sample media. The other methods had more than 50% of the elemental concentrations below

10x the detection limit and so these were not considered. The average percentage of duplicates within $\pm 25\%$ of percentage relative difference across all datasets was 80%, which although slightly lower than the 90% criteria, it demonstrates consistency across the dataset and reflects a level of reproducibility acceptable for use.

The 4AWR 2003-04 dataset met the second QC criterion with an average percentage relative difference less than $\pm 25\%$ (Table 4). For the 2006-07 datasets, the 4AWR, 4BWR analytical methods met the second QC criterion as they all showed an average percentage relative difference less than $\pm 25\%$ (Table 4). In contrast, 1FMS with an average of average percentage relative difference of 32% was in excess of $\pm 25\%$ limit and so does not meet the second criterion.

However, when the graphs are observed, it seems likely that this is due to a combination of the inherent inaccuracies in data measurement close to 10x the detection limit and the absence of composite sampling method for this sampling campaign, leading to an emphasis of the inherent heterogeneity between two individual rock samples.

Overall, both the 2003-04 and 2006-07 data is acceptable for use, although care should be taken with observed concentrations close to 10x the detection limit for the 2006-07 dataset.

Summary of QA/QC Results

Rock samples were collected from the Collahuasi region in two campaigns. 1054 samples were collected in 2003-04 and 403 samples in 2006-07 (**Error! Reference source not found.**).

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The QA/QC assessment of the rock data shows that the dataset is of a high quality.

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1FMS	Group 1F-MS Ultratrace by Mass Spec	ICP Mass Spec analysis of a sample after Aqua Regia digestion for low to ultra low determination on soils, sediments and lean rocks	Both
4ALO	Group 4A Whole Rock by ICP (Loss of Ignition)	Weight difference after ignition at 1000 ^o c	Both
4ALC	Group 4A Whole Rock by ICP (LECO)	Total Carbon and Sulphur analysis by LECO	Both
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4BTD	Group 4B Total Trace Elements by ICP - MS	Rare earth and refractory elements are determined by ICP mass spectrometry following four acid digest (HCl-HF-HClO ₄ -HNO ₃)	2003-04 only
7TDA	Group 7 ICP & ICP-MS	Percentage level concentrations as determined by ICP emission spectrometry	2006-07 only

The analytes measured by each technique are summarised in Table 5.

Table 5: Summary of analytical techniques and elements analysed

Analytical Method	2003-04 Analytes	2006-07 Analytes Olivine Basalt	2006-07 Analytes Altered Alkali Andesite
4AWR	SiO ₂ , Al ₂ O ₃ , Fe ₂ O ₃ , MgO, CaO, Na ₂ O, K ₂ O, TiO ₂ , P ₂ O ₅ , MnO, Ba, Ni	SiO ₂ , Al ₂ O ₃ , Fe ₂ O ₃ , MgO, CaO, Na ₂ O, K ₂ O, TiO ₂ , P ₂ O ₅ , MnO, Ba, Cr ₂ O ₃ *	SiO ₂ , Al ₂ O ₃ , Fe ₂ O ₃ , MgO, CaO, Na ₂ O, K ₂ O, TiO ₂ , P ₂ O ₅ , MnO, Ba
4BWR	n/a	Nb, Rb, Sr, Th, U, Zr, Y, La, Ce	Nb, Rb, Sn, Sr, Th, U, Zr, Y, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu
7TDA	n/a	Ni	Ni
1FMS	n/a	As, Co, Cr, Ni, Pb, Sb, Zn	As, Au, Bi, Co, Cr, Cu, Ni, Pb, Sb, Zn
4ALO	n/a	LOI	LOI
4ALC	n/a	C	n/a
G3B-MS	n/a	n/a	Au

Standards

In order to evaluate the accuracy of each of the analytical methods used, three types of standards were used. 2003-04 data was analysed using the OREAS 44P certified reference material (CRM) standard whilst 2006-07 data was analysed using Altered Andesite Whole Rock and Alkali Olivine Basalt (OREAS 24P) secondary reference material (SRM) standards. These standards were inserted into each analytical run and the results compared against known performance gates using graphs.

Performance gates for the analytical methods were referenced for 66 analytes. Performance gates included:

- | | |
|----------------------------|---|
| 1) the mean of the CRM/SRM | 3) ± 2 standard deviation of the mean |
| 2) $\pm 25\%$ of the mean | 4) ± 3 standard deviation of the mean |

Ideally, 95% of all samples should fall between ± 2 standard deviations (warning lines), with 99% between ± 3 standard deviations (failure lines). The standard suggests that a batch of analyses has failed to reach the level of accuracy required if one or more samples lie outside the failure lines (red) or data for more than two standards fall outside any warning line (orange) (Figure 1).

To allow for the intrinsic heterogeneity of rock samples (which have variability in their mineralogy and hence chemistry) an additional pass-fail criterion was established. An element passed if ≥ 3 analysed standard samples for each element were outside $\pm 25\%$ of the mean for that standard. Elements below the detection limit were excluded from evaluation because the results were not reliable.

Graphs for each standard show the analytical results for the reference material plotted against the order of analytes (Figure 1).

The QA/QC result for standards analysed using each analytical method are summarised in Table 3. The 4BTD method was only used during the analysis of the 2003-04 data.

Table 6: Summary of QA/QC accuracy results for 2003-04 data, OREAS 44P standard and 2006-07 data, Alkali Altered Andesite and Olivine Basalt standards, grouped according to analytical method

Analytical Method	Percentage of elements meeting QC criterion		
	OREAS 44P (2003-04)	Olivine Basalt (2006-07)	Alkali Altered Andesite (2006-07)
4AWR	100%	100%	92%
4BWR	n/a	100%	100%
1FMS	n/a	50%	80%
4ALO	n/a	0%	100%
4ALC	n/a	100%	n/a
G3B-MS	n/a	n/a	100%
4BTD	n/a	-	-
7TDA	n/a	100%	100%

OREAS 44P

For 2003-04 data, analysed using the OREAS 44P standard, only the analytical method 4AWR was subject to QA/QC evaluation - this was to verify the findings of previous quality control assessment on this data by Christian Ihlenfeld.

For the 4AWR method, an evaluation of accuracy using the OREAS 44P standard showed that the majority of elements had $< \pm 10\%$ bias between their mean and the certified mean, with 100% of elements satisfying the QC pass-fail criterion. The level of accuracy of this dataset is high (Table 3).

Olivine Basalt

For 2006-07 data, the accuracy of 6 of the 7 analytical methods was evaluated using the Olivine Basalt standard (Figure 1). The standards for elements analysed using G3B-MS (Au, Pt, Pd) were not evaluated since there are no certified values for the standard using this method.

For the 4AWR, 4BWR and 7TDA analytical methods, an evaluation of accuracy using the Olivine Basalt standards show that the majority of elements had $<\pm 10\%$ bias between their mean and the certified mean, with 100% of elements satisfying the QC pass-fail criterion. The level of accuracy of these datasets is high (Table 3).

For the 4ALC, 100% of elements satisfied the QC pass-fail criterion. However the graphs of the elements analysed showed a negative bias. This is reflected in the percentage bias of the analysed elements which was greater than $\pm 10\%$. The 1FMS and 4ALO methods also showed a large percentage bias, above $\pm 10\%$.

The 1FMS method showed a negative bias across all the data analysed. This bias meant that cobalt, chromium, lead and zinc lay outside the QA/QC parameters, resulting in only 50% of elements satisfying the QC pass-fail criterion. However, all cases including those which lay outside the QA/QC parameters, showed a high standard of reproducibility. Although the percentage of elements meeting the QC criterion is lower than for 4AWR, 4BWR and 7TDA methods, it accurate enough for the data to be acceptable for use.

The 4ALO method gave results for oxygen only. This dataset shows a positive bias with two points lying outside the QA/QC parameters and led to the method failing to meet the QC pass-fail criterion. Overall the data are very consistent, suggesting a high level of reproducibility but a positive bias away from the mean (reflected in the large percentage bias).

This appears to be a feature of the Olivine Basalt standard as the bias is not reflected in the analysis of the Alkali Altered Andesite data using the same methods. Therefore, it is likely that the variability seen with the Olivine Basalt was associated with the standard used rather than the analytical method and so, the data produced using the 1FMS and 4ALO methods can be considered as acceptable for use overall.

Alkali Altered Andesite

The accuracy of 6 of the 7 analytical methods was evaluated using the Alkaline Altered Andesite standard (Figure 1). The standards for carbon and sulphur analysed using 4ALC were not evaluated because there are no certified values for Alkali Altered Andesite using this method.

The analytical methods, 4AWR, 4BWR, 1FMS, evaluated using the Alkali Altered Andesite standard had $<\pm 10\%$ bias between their mean and the certified mean with 80% or higher of elements satisfied the QC pass-fail criterion for these analytical methods (Table 3).

The 7TDA, 4ALO and G3B-MS methods had greater than $\pm 10\%$ bias, but nonetheless 100% of elements satisfy the QC pass-fail criterion.

Therefore data for the Alkaline Altered Andesite standards suggested that the data is highly accurate.

Overall, the QA/QC result for all standards suggests that the majority of the analytical methods used produce highly accurate data.

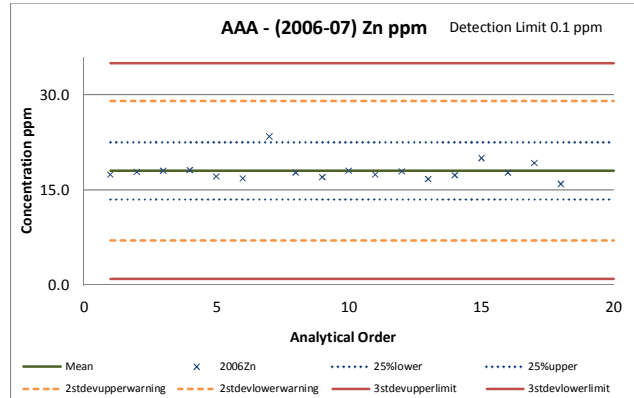
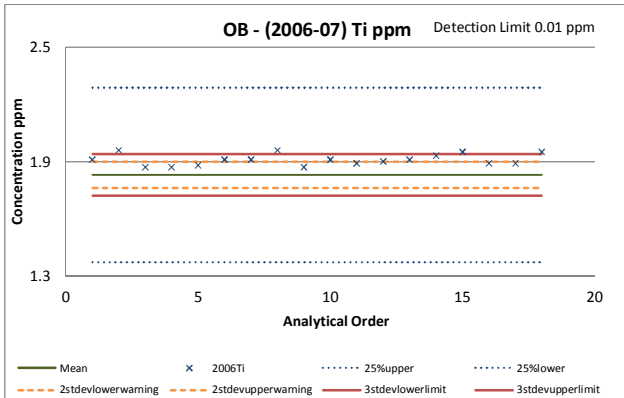
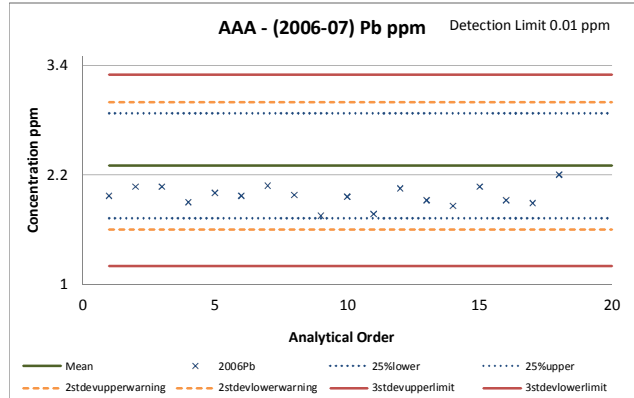
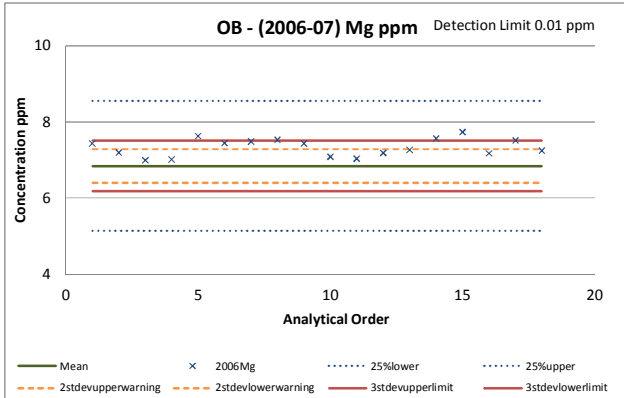
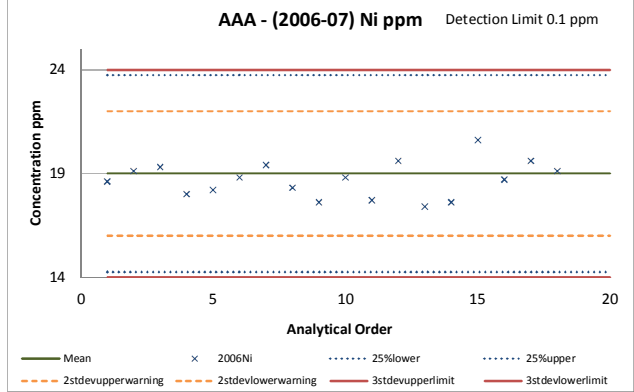
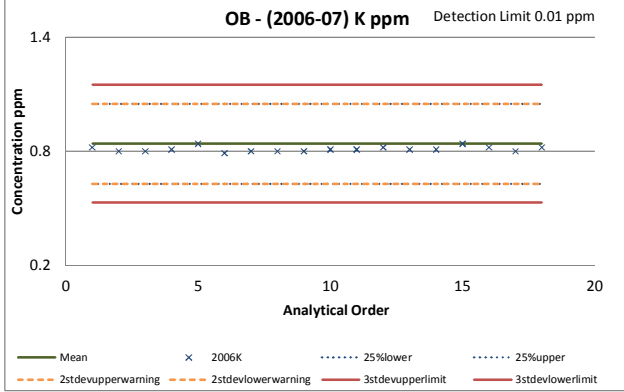
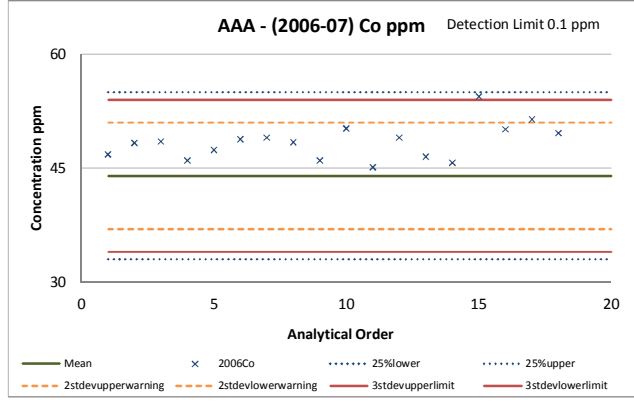
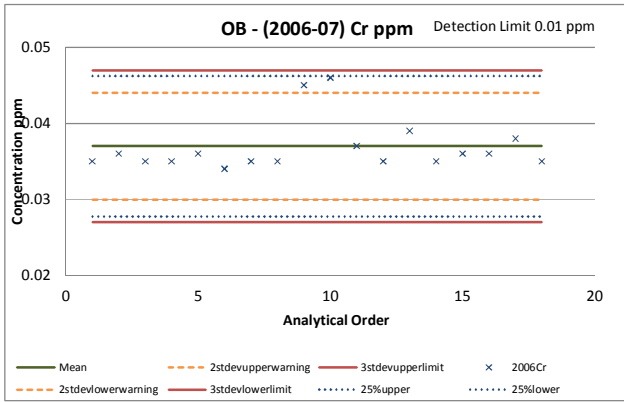


Figure 1: Collahuasi rocks, 2006-07, Standards Graphs.

LH = Olivine Basalt SRM, 4AWR Method, Cr, K, Mg, Ti.

RH = Alkali Altered Andesite SRM, 1FMS Method, Co, Ni, Pb, Zn.

Green line represents the reference mean of the SRM of the indicated element, dashed orange lines = ± 2 std dev., dashed red lines = ± 3 std dev., dashed blue lines = $\pm 25\%$ of mean.

(Collahuasi Rocks, 2003-04) Summary of accuracy assessments for the OREAS 44P CRM
Table 7: OREAS 44P – AWR
4AWR

Element	SiO ₂ %	Al ₂ O ₃ %	Fe ₂ O ₃ %	MgO %	CaO %	Na ₂ O %	K ₂ O %	TiO ₂ %	P ₂ O ₅ %	MnO %	Ba ppm	Ni ppm
Within 2 SD		x		x		x	x	x			x	
Within 3 SD												
Within ±25%	x		x		x							x
≤3 outside ±25%									x	x		
Outside Limits												
Evaluation												
mean 4AWR data	35.74	6.98	49.23	0.77	0.44	0.13	1.47	0.32	0.07	0.09	380.75	494.00
mean (OREAS44) certified	36.4	7.06	49.35	0.79	0.46	0.2	1.49	0.35	0.09	0.11	430	471
Bias ¹	-0.019	-0.011	-0.002	-0.032	-0.049	-0.375	-0.017	-0.079	-0.247	-0.159	-0.115	0.049
% Bias ²	-2	-1.1	-0.2	-3.16	-4.9	-37.50	-1.68	-7.9	-24.7	-15.9	-11.5	4.9
mean of data	68.04	14.23	4.08	0.94	1.36	3.06	2.79	0.52	0.12	0.06	627	20
detection limit	0.02	0.03	0.04	0.01	0.01	0.01	0.02	0.01	0.01	0.01	5	20
10x detection limit	0.2	0.3	0.4	0.1	0.1	0.1	0.2	0.1	0.1	0.1	50	200

Collahuasi (2003-04) OREAS 44P 4AWR Standard	
14	Total no. of elements evaluated
12	Total no. of elements meeting QC criterion^A
6	Elements within 2 sd of mean
6	Elements within 3 sd of mean
10	Elements within ±25% of mean
12	Elements with ≤3 points outside ±25% of mean
0	Total no. of elements not meeting QC criterion^B
0	Elements with ≥4 points outside ±25% of mean
0	Total no. of elements excluded from QC criterion
0	Elements below detection limit
0	Elements too close to detection limit
2	Elements with no certified values for S4³
% Elements Meeting Criterion*:	
*((A/(A+B))x100)	
	100%
% Elements within ±3 std dev and/or ±25 of mean:	
	83%

Colour Code for Bias	
	>10%
	5 to 10%
	2 to 5%
	-2 to 2%
	-2 to -5%
	-5 to -10%
	<-10%

$$^1 \text{ bias} = \frac{(x_{\text{data}} - x_{\text{standard}})}{x_{\text{standard}}}$$

$$^2 \text{ \% bias} = \text{bias} * 100$$

³ Cr, Sc

(Collahuasi Rocks, 2006-07) Summary of accuracy assessments for the Olivine Basalt SRM
Table 8: Olivine Basalt – 4AWR

Element	SiO ₂ %	Al ₂ O ₃ %	Fe ₂ O ₃ %	MgO %	CaO %	Na ₂ O %	K ₂ O %	TiO ₂ %	P ₂ O ₅ %	MnO %	Cr ₂ O ₃ %	Ba ppm
Within 2 SD						x	x		x	x		x
Within 3 SD			x					x			x	
Within ±25%	x	x		x	x							
≤3 outside ±25%												
Outside Limits												
Evaluation												
mean 4AWR data	51.1	14.27	11.28	7.33	8.61	3.14	0.81	1.91	0.32	0.15	0.037	273
mean (olivine basalt) certified	51.7	14.46	11.40	6.84	8.49	3.11	0.84	1.83	0.31	0.14	0.037	285
Bias ¹	-0.012	-0.013	-0.010	0.071	0.014	0.009	-0.034	0.043	0.013	0.060	-0.005	-0.041
% Bias ²	-1	-1.3	-1.0	7.12	1.4	0.95	-3.44	4.3	1.3	6.0	-0.5	-4.1
mean of data	69.68	13.32	4.78	1.01	1.44	3.73	3.73	0.51	0.14	0.12	0.003	764
detection limit	0.02	0.03	0.04	0.01	0.01	0.01	0.04	0.01	0.01	0.01	0.001	5
10x detection limit	100	100	100	50	60	50	50	100	50	50	100	50000

Collahuasi (2006-07) Olivine Basalt 4AWR Standard	
13	Total no. of elements evaluated
12	Total no. of elements meeting QC criterion^A
5	Elements within 2 sd of mean
8	Elements within 3 sd of mean
12	Elements within ±25% of mean
12	Elements with ≤3 points outside ±25% of mean
0	Total no. of elements not meeting QC criterion^B
0	Elements with ≥4 points outside ±25% of mean
0	Total no. of elements excluded from QC criterion
0	Elements below detection limit
0	Elements too close to detection limit
1	Elements with no certified values for S4³
% Elements Meeting Criterion*:	
*((A/(A+B))x100)	
	100%
% Elements within ±3 std dev and/or ±25 of mean:	
	100%

Colour Code for Bias	
	>10%
	5 to 10%
	2 to 5%
	-2 to 2%
	-2 to -5%
	-5 to -10%
	<-10%

$$^1 \text{ bias} = ((x_{\text{data}} - x_{\text{standard}})/x_{\text{standard}})$$

$$^2 \text{ \% bias} = \text{bias} * 100$$

³ Sc

Table 9: Olivine Basalt – 4BWR

Element	Nb_ppm	Rb_ppm	Sr_ppm	Th_ppm	U_ppm	Zr_ppm	Y_ppm	La_ppm	Ce_ppm
Within 2 SD	x			x	x	x		x	
Within 3 SD									
Within ±25%		x	x				x		x
≤3 outside ±25%									
Outside Limits									
Evaluation									
mean 4BWR data	19.9	20.62	412.34	2.70	0.69	138.79	23.78	16.66	35.01
mean (olivine basalt) certified	21.0	22.40	403.00	2.85	0.75	141	22.90	17.40	37.60
Bias ¹	-0.054	-0.079	0.023	-0.053	-0.074	-0.016	0.038	-0.042	-0.069
% Bias ²	-5	-7.9	2.3	-5.26	-7.4	-1.57	3.83	-4.2	-6.9
mean of data	10.10	125.38	144.56	13.28	3.10	196.21	35.52	26.78	58.23
detection limit	0.5	0.5	0.5	0.1	0.1	0.5	0.1	0.5	0.5
10x detection limit	5	5	5	1	1	5	1	5	5

Collahuasi (2006-07) Olivine Basalt 4BWR Standard	
9	Total no. of elements evaluated
9	Total no. of elements meeting QC criterion^A
5	Elements within 2 sd of mean
5	Elements within 3 sd of mean
9	Elements within ±25% of mean
9	Elements with ≤3 points outside ±25% of mean
0	Total no. of elements not meeting QC criterion^B
0	Elements with ≥4 points outside ±25% of mean
0	Total no. of elements excluded from QC criterion
0	Elements below detection limit
0	Elements too close to detection limit
19	Elements with no certified values for S4³
% Elements Meeting Criterion*: *((A/(A+B))*100)	
	100%
% Elements within ±3 std dev and/or ±25 of mean:	
	100%

Colour Code for Bias	
	>10%
	5 to 10%
	2 to 5%
	-2 to 2%
	-2 to -5%
	-5 to -10%
	<-10%

¹ bias = ((x̄data - x̄standard)/x̄standard)
² % bias = bias *100

³ Cs, Ga, Hf, Sn, Ta, V, W, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu

Table 10: Olivine Basalt – 4ALC

Element	TOT/C_%	TOT/S_%
Within 2 SD		
Within 3 SD	x	
Within ±25%		
≤3 outside ±25%		
Outside Limits		
Evaluation		below det.
mean 4ALC data	0.05	0.01
mean (olivine basalt) certified	0.08	0.01
Bias ¹	-0.42	-0.14
% Bias ²	-42	-14
mean of data	1.5	1.5
detection limit	0.1	0.1
10x detection limit	1.0	1.0

Collahuasi (2006-07) Olivine Basalt 4ALC Standard	
2	Total no. of elements evaluated
1	Total no. of elements meeting QC criterion ^A
0	Elements within 2 sd of mean
1	Elements within 3 sd of mean
0	Elements within ±25% of mean
0	Elements with ≤3 points outside ±25% of mean
0	Total no. of elements not meeting QC criterion ^B
0	Elements with ≥4 points outside ±25% of mean
1	Total no. of elements excluded from QC criterion
1	Elements below detection limit
0	Elements too close to detection limit
0	Elements with no certified values for S4 ³
% Elements Meeting Criterion*: $\frac{1}{((A/(A+B)) \times 100)}$	
	100%
% Elements within ±3 std dev and/or ±35 of mean:	
	100%

Colour Code for Bias	
	>10%
	5 to 10%
	2 to 5%
	-2 to 2%
	-2 to -5%
	-5 to -10%
	<-10%

¹ bias = $\frac{(x \text{ data} - x \text{ standard})}{x \text{ standard}}$
² % bias = bias * 100

Table 11: Olivine Basalt – 7TDA

Element	TOT/C_%	TOT/S_%
Within 2 SD		
Within 3 SD	x	
Within ±25%		
≤3 outside ±25%		
Outside Limits		
Evaluation		below det.
mean 4ALC data	0.05	0.01
mean (olivine basalt) certified	0.08	0.01
Bias ¹	-0.42	-0.14
% Bias ²	-42	-14
mean of data	1.5	1.5
detection limit	0.1	0.1
10x detection limit	1.0	1.0

Collahuasi (2006-07) Olivine Basalt 7TDA Standard	
1	Total no. of elements evaluated
1	Total no. of elements meeting QC criterion ^A
1	Elements within 2 sd of mean
1	Elements within 3 sd of mean
1	Elements within ±25% of mean
1	Elements with ≤3 points outside ±25% of mean
0	Total no. of elements not meeting QC criterion ^B
0	Elements with ≥4 points outside ±25% of mean
0	Total no. of elements excluded from QC criterion
0	Elements below detection limit
0	Elements too close to detection limit
0	Elements with no certified values for S4
% Elements Meeting Criterion*: $\frac{1}{((A/(A+B)) \times 100)}$	
	100%
% Elements within ±3 std dev and/or ±35 of mean:	
	100%

Colour Code for Bias	
	>10%
	5 to 10%
	2 to 5%
	-2 to 2%
	-2 to -5%
	-5 to -10%
	<-10%

¹ bias = $\frac{(x \text{ data} - x \text{ standard})}{x \text{ standard}}$
² % bias = bias * 100

Table 12: Olivine Basalt – 4ALO
4ALO

Element	LOI_%
Within 2 SD	
Within 3 SD	
Within ±25%	
≤3 outside ±25%	
Outside Limits	x
Evaluation	2 outside >±25%†
mean 4ALO data	1.0
mean (olivine basalt) certified	0.6
Bias ¹	0.61
% Bias ²	61
mean of data	1.5
detection limit	0.1
10x detection limit	1.0

Collahuasi (2006-07) Olivine Basalt 4ALO Standard	
1	Total no. of elements evaluated
0	Total no. of elements meeting QC criterion ^A
0	Elements within 2 sd of mean
0	Elements within 3 sd of mean
0	Elements within ±25% of mean
0	Elements with ≤3 points outside ±25% of mean
1	Total no. of elements not meeting QC criterion ^B
1	Elements with ≥4 points outside ±25% of mean
0	Total no. of elements excluded from QC criterion
0	Elements below detection limit
0	Elements too close to detection limit
0	Elements with no certified values for S4
% Elements Meeting Criterion*: $\frac{1}{((A/(A+B)) \times 100)}$	
	0%
% Elements within ±3 std dev and/or ±35 of mean:	
	0%

Colour Code for Bias	
	>10%
	5 to 10%
	2 to 5%
	-2 to 2%
	-2 to -5%
	-5 to -10%
	<-10%

¹ bias = $\frac{(x \text{ data} - x \text{ standard})}{x \text{ standard}}$
² % bias = bias * 100

Table 12: Olivine Basalt – 1FMS

Element	As_ppm	Co_ppm	Cr_ppm	Cu_ppm	Ni_ppm	Pb_ppm	Sb_ppm	Zn_ppm
Within 2 SD	x						x	
Within 3 SD				x				
Within ±25%					x			
≤3 outside ±25%								
Outside Limits		x	x			x		x
Evaluation		all points outside ±25%	all points outside ±25%			all points outside >±25%†		all points outside ±25%
mean 1FMS data	0.3	30.7	27.4	40.18	117.2	0.84	0.05	70.1
mean (olivine basalt) certified	2.0	44	221	52	141	2.9	0.14	114
Bias ¹	-0.86	-0.30	-0.88	-0.23	-0.17	-0.71	-0.65	-0.39
% Bias ²	-86	-30.2	-87.6	-22.73	-16.9	-71.05	-64.68	-38.5
mean of data	20.3	5.9	10.4	203.62	4.1	47.43	1.61	254.2
detection limit	0.1	0.1	0.5	0.01	0.1	0.01	0.02	0.1
10x detection limit	1.0	1.0	5.00	0.10	1.0	0.10	0.20	1.0

Collahuasi (2006-07) Olivine Basalt 1FMS Standard	
26	Total no. of elements evaluated
4	Total no. of elements meeting QC criterion ^A
2	Elements within 2 sd of mean
3	Elements within 3 sd of mean
4	Elements within ±25% of mean
4	Elements with ≤3 points outside ±25% of mean
4	Total no. of elements not meeting QC criterion ^B
4	Elements with ≥4 points outside ±25% of mean
0	Total no. of elements excluded from QC criterion
0	Elements below detection limit
0	Elements too close to detection limit
18	Elements with no certified values for S4 ³
% Elements Meeting Criterion*:	50%
*(A/(A+B))*100	
% Elements within ±3 std dev and/or ±35 of mean:	50%

Colour Code for Bias	
	>10%
	5 to 10%
	2 to 5%
	-2 to 2%
	-2 to -5%
	-5 to -10%
	<-10%

¹ bias =
 $(\bar{x}_{data} - \bar{x}_{standard}) / \bar{x}_{standard}$

² % bias = bias * 100

³ Mo, Ag, Mn, Au, Cd, Bi, B, Tl, Hg, Se, Te, Ge, In, Re, Be, Li, Pd, Pt

(Collahuasi Rocks) Summary of accuracy assessments for the Alkali Altered Andesite SRM
Table 13: Alkali Altered Andesite – AWR

Element	SiO ₂ _%	Al ₂ O ₃ _%	Fe ₂ O ₃ _%	MgO_%	CaO_%	Na ₂ O_%	K ₂ O_%	TiO ₂ _%	P ₂ O ₅ _%	MnO_%	Ba_ppm
Within 2 SD	x	x	x			x		x		x	x
Within 3 SD					x						
Within ±25%				x			x				
≤3 outside ±25%											
Outside Limits									x		
Evaluation									2 outside >±25%†		
mean 4AWR data	57.5	16.50	10.94	3.05	0.09	0.27	7.66	0.68	0.04	0.05	1092
mean (alkali altered andesite) certified	57.5	16.18	10.73	2.95	0.10	0.27	8.25	0.68	0.03	0.05	1094
Bias ¹	-0.001	0.020	0.019	0.035	-0.139	0.004	-0.072	0.005	0.204	0.000	-0.002
% Bias ²	0	2.0	1.9	3.52	-13.9	0.41	-7.21	0.5	20.4	0.0	-0.2
mean of data	69.68	13.32	4.78	1.01	1.44	3.73	3.73	0.51	0.14	0.12	763
detection limit	0.02	0.03	0.04	0.01	0.01	0.01	0.04	0.01	0.01	0.01	5
10x detection limit	100	100	100	50	60	50	50	100	50	50	50000

Collahuasi (2006-07) Altered Andesite 4AWR Standard	
13	Total no. of elements evaluated
12	Total no. of elements meeting QC criterion^A
7	Elements within 2 sd of mean
8	Elements within 3 sd of mean
10	Elements within ±25% of mean
10	Elements with ≤3 points outside ±25% of mean
1	Total no. of elements not meeting QC criterion^B
1	Elements with ≥4 points outside ±25% of mean
0	Total no. of elements excluded from QC criterion
0	Elements below detection limit
0	Elements too close to detection limit
2	Elements with no certified values for S₄³
% Elements Meeting Criterion*: $\frac{A}{(A+B)} \times 100$	
	92%
% Elements within ±3 std dev and/or ±25 of mean:	
	77%

Colour Code for Bias	
	>10%
	5 to 10%
	2 to 5%
	-2 to 2%
	-2 to -5%
	-5 to -10%
	<-10%

¹ bias = $\frac{(x_{data} - x_{standard})}{x_{standard}}$

² % bias = bias * 100

³ Cr, Sc

Table 14: Alkali Altered Andesite – 1FMS

Element	As_ppm	Au_ppb	Bi_ppm	Co_ppm	Cr_ppm	Cu_ppm	Ni_ppm	Pb_ppm	Sb_ppm	Zn_ppm
Within 2 SD		x	x		x		x	x		x
Within 3 SD										
Within ±25%				x						
≤3 outside ±25%						x				
Outside Limits	x								x	
Evaluation	4 outside >±25%†								all points outside >±25%†	
mean 1FMS data	3.1	19.8	0.10	48.4	28.8	418.20	18.7	1.97	0.75	18.0
mean (altered andesite) certified	6.0	20.0	0.09	44	30	430	19	2.3	1.4	18
Bias ¹	-0.48	-0.01	0.07	0.10	-0.04	-0.03	-0.02	-0.14	-0.47	0.00
% Bias ²	-48	-0.9	6.79	10.0	-4.1	-2.74	-1.6	-14.42	-46.71	-0.2
mean of data	20.3	4.8	0.59	5.9	10.4	203.62	4.1	47.43	1.61	254.2
detection limit	0.1	0.2	0.02	0.1	0.5	0.01	0.1	0.01	0.02	0.1
10x detection limit	1.0	2.0	0.20	1.0	5.00	0.10	1.0	0.10	0.20	1.0

Collahuasi (2006-07) Altered Andesite 1FMS Standard	
26	Total no. of elements evaluated
8	Total no. of elements meeting QC criterion^A
6	Elements within 2 sd of mean
6	Elements within 3 sd of mean
7	Elements within ±25% of mean
8	Elements with ≤3 points outside ±25% of mean
2	Total no. of elements not meeting QC criterion^B
2	Elements with ≥4 points outside ±25% of mean
0	Total no. of elements excluded from QC criterion
0	Elements below detection limit
0	Elements too close to detection limit
16	Elements with no certified values for S4³
% Elements Meeting Criterion*:	
*((A/(A+B))x100)	
	80%
% Elements within ±3 std dev and/or ±25 of mean:	
	70%

Colour Code for Bias	
	>10%
	5 to 10%
	2 to 5%
	-2 to 2%
	-2 to -5%
	-5 to -10%
	<-10%

$$^1 \text{ bias} = \frac{(x_{\text{data}} - x_{\text{standard}})}{x_{\text{standard}}}$$

$$^2 \% \text{ bias} = \text{bias} * 100$$

³ Mo, Ag, Mn, Cd, Ti, Tl, Hg, Se, Te, Ge, In, Re, Be, Ii, Pd, Pt

Table 15: Alkali Altered Andesite – 4BWR

Element	Nb_ppm	Rb_ppm	Sn_ppm	Sr_ppm	Th_ppm	U_ppm	Zr_ppm	Y_ppm	La_ppm	Ce_ppm	Pr_ppm
Within 2 SD	x		x	x	x	x	x				x
Within 3 SD									x	x	
Within ±25%		x						x			
≤3 outside ±25%											
Outside Limits											
Evaluation											
mean 4BWR data	3.5	183.13	4.39	44.86	4.22	1.08	120.37	9.52	3.63	7.01	0.875
mean (altered andesite) certified	4.0	202.00	5.00	46.00	4.5	1.20	129	9.20	4.00	7.40	0.9
Bias ¹	-0.118	-0.093	-0.122	-0.025	-0.063	-0.097	-0.067	0.035	-0.093	-0.053	-0.028
% Bias ²	-12	-9.3	-12.2	-2.5	-6.30	-9.7	-6.69	3.50	-9.3	-5.3	-2.8
mean of data	10.12	125.23	2.20	144.83	13.30	3.10	196.42	35.59	26.85	58.36	6.886703
detection limit	0.5	0.5	1	0.5	0.1	0.1	0.5	0.1	0.5	0.5	0.02
10x detection limit	5	5	10	5	1	1	5	1	5	5	0.2
Element	Nd_ppm	Sm_ppm	Eu_ppm	Gd_ppm	Tb_ppm	Dy_ppm	Ho_ppm	Er_ppm	Tm_ppm	Yb_ppm	Lu_ppm
Within 2 SD	x	x	x	x	x				x	x	
Within 3 SD						x		x			
Within ±25%							x				x
≤3 outside ±25%											
Outside Limits											
Evaluation											
mean 4BWR data	3.73	1.0	0.24	1.19	0.24	1.39	0.29	0.89	0.15	0.99	0.16
mean (altered andesite) certified	3.7	1.0	0.20	1.20	0.22	1.5	0.30	1	0.16	1.10	0.19
Bias ¹	0.009	-0.019	0.217	-0.006	0.083	-0.076	-0.043	-0.108	-0.087	-0.099	-0.167
% Bias ²	1	-2	21.7	-0.6	8.3	-7.56	-4.3	-10.78	-8.68	-9.9	-16.7
mean of data	27.23	5.50	1.03	5.14	0.96	5.32	1.06	3.28	0.53	3.46	0.52
detection limit	0.4	0.1	0.05	0.05	0.01	0.05	0.05	0.05	0.05	0.05	0.01
10x detection limit	4	1	0.5	0.5	0.1	0.5	0.5	0.5	0.5	0.5	0.1

Collahuasi (2006-07) Altered Andesite 4BWR Standard	
22	Total no. of elements evaluated
22	Total no. of elements meeting QC criterion^A
14	Elements within 2 sd of mean
18	Elements within 3 sd of mean
22	Elements within ±25% of mean
22	Elements with ≤3 points outside ±25% of mean
0	Total no. of elements not meeting QC criterion^B
0	Elements with ≥4 points outside ±25% of mean
0	Total no. of elements excluded from QC criterion
0	Elements below detection limit
0	Elements too close to detection limit
6	Elements with no certified values for S4³
% Elements Meeting Criterion*:	
*((A/(A+B))*100)	
	100%
% Elements within ±3 std dev and/or ±25 of mean:	
	100%

Colour Code for Bias	
	>10%
	5 to 10%
	2 to 5%
	-2 to 2%
	-2 to -5%
	-5 to -10%
	<-10%

¹ bias =
 $(x \text{ data} - x \text{ standard}) / x \text{ standard}$
² % bias = bias * 100

Table 16: Alkali Altered Andesite – 7TDA

Element	Ni_ppm
Within 2 SD	
Within 3 SD	
Within ±25%	
≤3 outside ±25%	x
Outside Limits	
Evaluation	
mean 7TDA data	17.0
mean (altered andesite) certified	19
Bias ¹	-0.11
% Bias ²	-10.5
mean of data	7.1
detection limit	0.1
10x detection limit	1.0

Collahuasi (2006-07) Altered Andesite 7TDA Standard	
1	Total no. of elements evaluated
1	Total no. of elements meeting QC criterion ^A
0	Elements within 2 sd of mean
0	Elements within 3 sd of mean
0	Elements within ±25% of mean
1	Elements with ≤3 points outside ±25% of mean
0	Total no. of elements not meeting QC criterion ^B
0	Elements with ≥4 points outside ±25% of mean
0	Total no. of elements excluded from QC criterion
0	Elements below detection limit
0	Elements too close to detection limit
0	Elements with no certified values for S4
% Elements Meeting Criterion*: $\frac{A}{(A+B)} \times 100$	
100%	
% Elements within ±3 std dev and/or ±25 of mean: 0	

Colour Code for Bias	
	>10%
	5 to 10%
	2 to 5%
	-2 to 2%
	-2 to -5%
	-5 to -10%
	<-10%

¹ bias = $\frac{(x \text{ data} - x \text{ standard})}{x \text{ standard}}$
² % bias = bias * 100

Table 17: Alkali Altered Andesite – 4ALO

Element	LOI %
Within 2 SD	
Within 3 SD	
Within ±25%	x
≤3 outside ±25%	
Outside Limits	
Evaluation	
mean 4ALO data	3.2
mean (altered andesite) certified	2.9
Bias ¹	0.13
% Bias ²	13
mean of data	1.5
detection limit	0.1
10x detection limit	1.0

Collahuasi (2006-07) Altered Andesite 4ALO Standard	
1	Total no. of elements evaluated
1	Total no. of elements meeting QC criterion ^A
0	Elements within 2 sd of mean
0	Elements within 3 sd of mean
1	Elements within ±25% of mean
1	Elements with ≤3 points outside ±25% of mean
0	Total no. of elements not meeting QC criterion ^B
0	Elements with ≥4 points outside ±25% of mean
0	Total no. of elements excluded from QC criterion
0	Elements below detection limit
0	Elements too close to detection limit
0	Elements with no certified values for S4
% Elements Meeting Criterion*: $\frac{A}{(A+B)} \times 100$	
100%	
% Elements within ±3 std dev and/or ±25 of mean: 100%	

Colour Code for Bias	
	>10%
	5 to 10%
	2 to 5%
	-2 to 2%
	-2 to -5%
	-5 to -10%
	<-10%

¹ bias = $\frac{(x \text{ data} - x \text{ standard})}{x \text{ standard}}$
² % bias = bias * 100

Table 18: Alkali Altered Andesite – G3B-MS

Element	Au_ppb
Within 2 SD	
Within 3 SD	
Within ±25%	
≤3 outside ±25%	x
Outside Limits	
Evaluation	
mean G3B-MS data	15.9
mean (altered andesite) certified	20
Bias ¹	-0.21
% Bias ²	-20.56
mean of data	6.4
detection limit	0.2
10x detection limit	2.0

Collahuasi (2006-07) Altered Andesite G3B-MS Standard	
3	Total no. of elements evaluated
1	Total no. of elements meeting QC criterion ^A
0	Elements within 2 sd of mean
0	Elements within 3 sd of mean
0	Elements within ±25% of mean
1	Elements with ≤3 points outside ±25% of mean
0	Total no. of elements not meeting QC criterion ^B
0	Elements with ≥4 points outside ±25% of mean
0	Total no. of elements excluded from QC criterion
0	Elements below detection limit
0	Elements too close to detection limit
2	Elements with no certified values for S4 ³
% Elements Meeting Criterion*: $\frac{A}{(A+B)} \times 100$	
100%	
% Elements within ±3 std dev and/or ±25 of mean: 0%	

Colour Code for Bias	
	>10%
	5 to 10%
	2 to 5%
	-2 to 2%
	-2 to -5%
	-5 to -10%
	<-10%

¹ bias = $\frac{(x \text{ data} - x \text{ standard})}{x \text{ standard}}$
² % bias = bias * 100

³ Pd, Pt

Field Duplicates

During the sampling campaigns, field duplicates were collected to determine the sampling variation (Table 1).

In order to evaluate the precision of the data collected, the percentage relative difference between duplicates was calculated for each analytical method.

The duplicate results are presented as graphs for each chemical element, comparing the percentage relative difference plotted against the original-duplicate mean (1).

$$y\text{-axis: } \frac{\text{Original} - \text{Duplicate}}{\frac{1}{2}(\text{Original} + \text{Duplicate})} \times 100 \quad (1)$$

$$x\text{-axis: } \frac{1}{2}(\text{Original} + \text{Duplicate})$$

Two pass-fail criteria were applied to each element;

- 1) An element passed where 90% of values fell within $\pm 25\%$ of the percentage relative difference
- 2) The entire dataset passed if the average percentage relative difference of all analytes was $< \pm 25\%$ *

A black solid line which represents ten times the detection limit is plotted parallel to Y axis (Figure 2) or otherwise indicated. Samples less than 10 times the detection limit and elements where more than 50% of samples were less than 10 times the detection limit were excluded from the evaluation.

*Elements with sample concentrations close to detection limits show increased variability resulting from difficulties maintaining accuracy of measurements at low concentrations. The second pass-fail criterion accounts for this by considering the overall average percentage relative difference per element; this reflects the overall behaviour of the dataset and so minimises the variability caused by samples close to the detection limits.

Table 4: Summary of QA/QC reproducibility results for duplicates, grouped according to dataset and analytical method

Analytical Method	Percentage of elements meeting first QC Criterion		Percentage of elements meeting second Criterion	
	(1) % duplicates with $\geq 90\%$ samples within $\pm 25\%$ of percentage relative difference		(2) Average of average percentage relative difference	
	2003-04	2006-07	2003-04	2006-07
4AWR	100%	46%	2%	10%
4BWR	-	50%	-	11%
1FMS	-	0%	-	32%
7TDA	-	below 10x DL	-	below 10x DL
4ALO	-	below 10x DL	-	below 10x DL
4ALC	-	below 10x DL	-	below 10x DL
G3B-MS	-	below 10x DL	-	below 10x DL

(1) Percentage of duplicates with $\geq 90\%$ of samples within $\pm 25\%$ of percentage relative difference (meeting first QC criterion)

For all analytical methods used to analyse the Collahuasi 2003-04 rock samples, the percentage of duplicates with $\geq 90\%$ samples falling within $\pm 25\%$ of relative difference was 100% (Table 4).

For the analytical methods used to analyse the Collahuasi 2006-07 rock samples, the percentage of duplicates with $\geq 90\%$ for 4AWR, 4BWR and 1FMS methods was 46%, 50% and 0% respectively (Figure 3). The other methods had more than 50% of the elemental concentrations below 10x the detection limit and so these were not considered.

This performance of 4AWR and 4BWR is low at approximately 50% however this is thought to reflect the inherent heterogeneity of rock samples and the high variability of the sample media. The chemistry of rocks may vary significantly over mm distance as a result of the changing mineralogy and varied states (e.g. oxidised, reduced) in which elements may be present. However, the average percentage of duplicates within $\pm 25\%$ of percentage relative difference across all datasets was 80%. Although this is lower than the 90% criteria, it demonstrates consistency across the dataset and reflects a level of reproducibility acceptable for use.

To allow for the intrinsic heterogeneity of rock samples an additional pass-fail criterion was established. An element passed if 3 analysed standard samples for each element were outside $\pm 25\%$ of the mean for that standard.

(2) Average of average percentage relative difference (meeting second QC criterion)

The 4AWR 2003-04 dataset met the second QC criterion with an average percentage relative difference less than $\pm 25\%$ (Table 4).

For the 2006-07 datasets, the 4AWR, 4BWR analytical methods met the second QC criterion as they all showed an average percentage relative difference less than $\pm 25\%$ (Table 4). In contrast, 1FMS with an average of average percentage relative difference of 32% was in excess of $\pm 25\%$ limit and so does not meet the second criterion.

However, when the graphs are observed, many of the elements have concentrations outside of the limits are clustered close to the 10x detection limit (Figure 2) so it is possible that it is inaccuracies in measurement at low concentrations which cause the slightly greater average relative difference than desired. Additionally, it is thought that the original sampling for this dataset did not use a composite sampling method, without which it is difficult to take accurately reproducible rock samples due to the inherent heterogeneity of individual rock units. Therefore, although higher than the ideal, the average relative difference is low enough for the data to be accepted for use, as long as care is taken with observed concentrations close to 10x the detection limit.

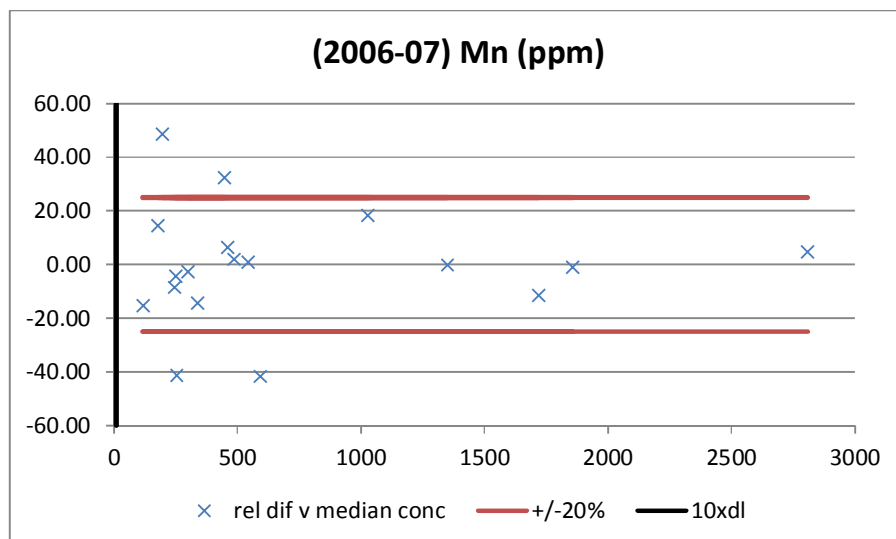


Figure 2 - illustrating the clustering of concentrations outside of desired limits near to the 10x detection limit

The datasets for 7TDA, 4ALO, 4ALC and G3B-MS methods contained elements which were below 10x detection limit and therefore were excluded from QA/QC evaluation.

Overall, although the performance of the datasets under the first criterion was low, the performance against the second criterion suggests that this reflects the intrinsic heterogeneity of the rock samples and low concentrations close to 10x detection limit.

Overall, the data is acceptable for use.

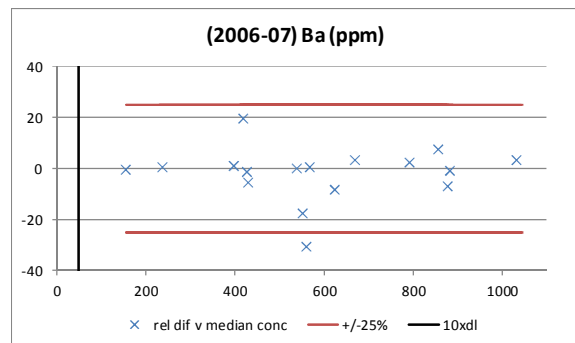
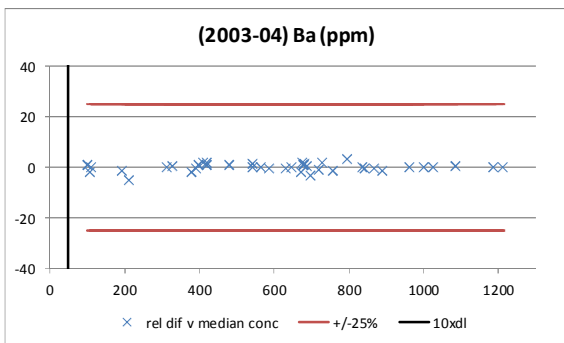
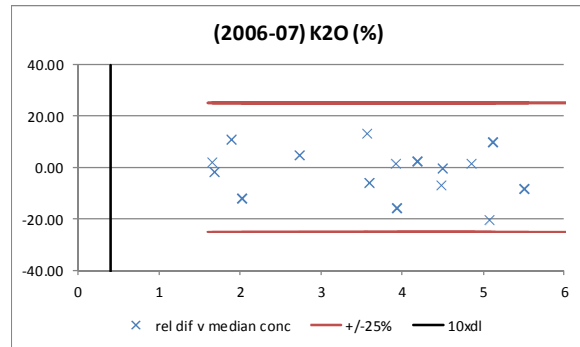
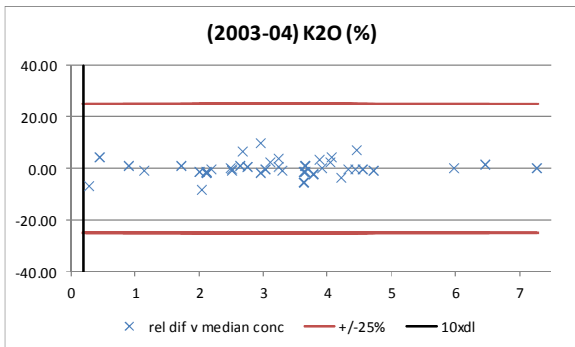
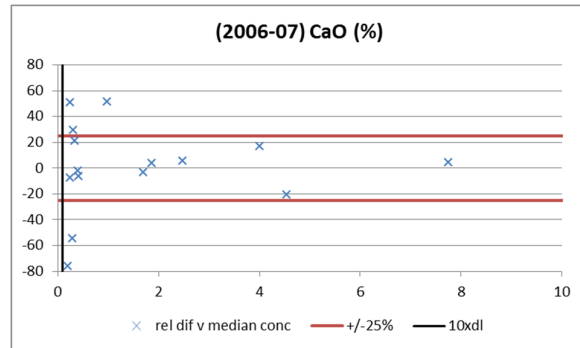
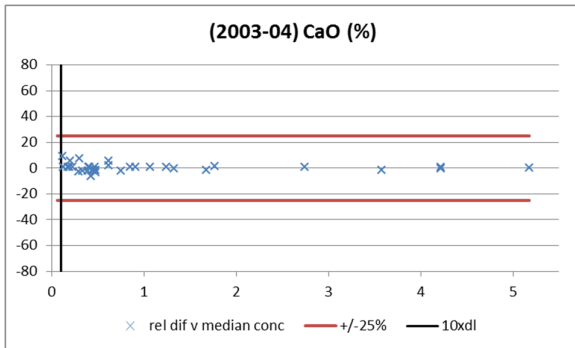
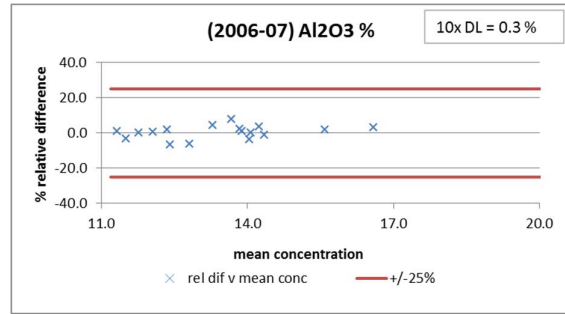
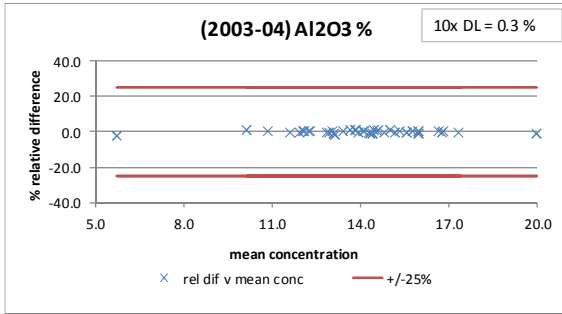
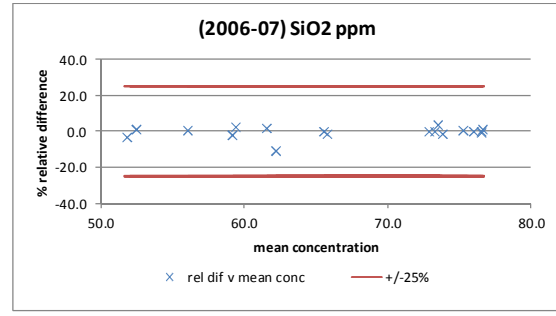
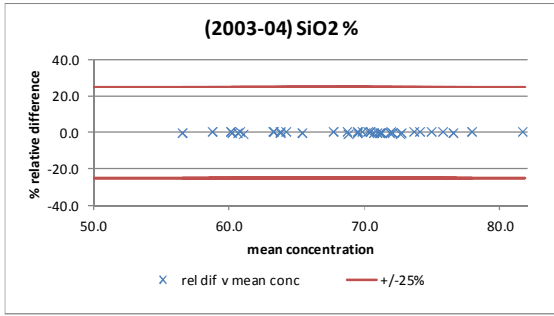


Figure 3: Collahuasi Rocks – Duplicates Graphs. Horizontal red lines represent $\pm 25\%$ error margins. Vertical black lines represent ten times the detection limit for each element.

LH side: Collahuasi 2003-04 Rocks, RH side Collahuasi 2006-07 Rocks, both 4AWR Method, Si, Al, Ca, K, Ba

(Collahuasi 2003-04 Rocks) Reproducibility assessment for field duplicates
Table 19: 4AWR

Element	SiO2 (%)	Al2O3 (%)	Fe2O3 (%)	MgO (%)	CaO (%)	Na2O (%)	K2O (%)	TiO2 (%)	P2O5 (%)	MnO (%)	Cr2O3 (%)	Ba (ppm)	Sc (ppm)	Ni (ppm)
10x det. limit	0.2	0.3	0.4	0.1	0.1	0.1	0.4	0.1	0.1	0.1	0.01	50	10	200
no samples outside ±25%	0	0	0	0	0	0	0	0				0		
% within error	100	100	100	100	100	100	100	100				100		
≥90% data within ±25%	x	x	x	x	x	x	x	x				x		
samples <10x det. limit									x	x	x		x	x
<90% within ±25%														
Average % relative difference	0.3	0.6	2.1	1.0	3.0	3.0	2.0	1.0	N/A	N/A	N/A	1.0	N/A	N/A

Collahuasi (2003-04) 4AWR Duplicates - Summary	
14	Total no. of elements evaluated
9	Total no. of elements meeting QC criteria^A
9	≥90% duplicates within ±25% of %relative difference
0	Total no. of elements not meeting QC criteria^B
0	<90% duplicates within ±25% of %relative difference
5	Total no. of elements excluded from QC criteria
5	>50% of samples below 10x detection limit
(1) % duplicates with ≥90% samples within ±25% of relative difference $((A/(A+B)) \times 100)$	100%
(2) Average of average % relative difference:	2%

(Collahuasi 2006-07 Rocks) Reproducibility assessment for field duplicates
Table 20: 4AWR

Element	SiO2 (%)	Al2O3 (%)	Fe2O3 (%)	MgO (%)	CaO (%)	Na2O (%)	K2O (%)	TiO2 (%)	P2O5 (%)	MnO (%)	Cr2O3 (%)	Ba (ppm)	Sc (ppm)
10x det. limit	0.2	0.3	0.4	0.1	0.1	0.1	0.4	0.1	0.1	0.1	0.01	50	10
no samples outside ±25%	0	0	2	4	5	2	0	1	2			0	0
% within error	100	100	89	69	69	89	100	92	80			100	100
≥90% data within ±25%	x	x					x	x				x	x
samples <10x det. limit										x	x		
<90% within ±25%			x	x	x	x			x				
Average % relative difference	2	3	11	24	23	11	7	5	13	N/A	N/A	6	6

Collahuasi (2006-07) 4AWR Duplicates - Summary	
13	Total no. of elements evaluated
6	Total no. of elements meeting QC criteria^A
6	≥90% duplicates within ±25% of %relative difference
5	Total no. of elements not meeting QC criteria^B
5	<90% duplicates within ±25% of %relative difference
2	Total no. of elements excluded from QC criteria
2	>50% of samples below 10x detection limit
(1) % duplicates with ≥90% samples within ±25% of relative difference $((A/(A+B)) \times 100)$	46%
(2) Average of average % relative difference:	10%

Table 21: 4BWR

Element	Cs (ppm)	Ga (ppm)	Hf (ppm)	Nb (ppm)	Rb (ppm)	Sn (ppm)	Sr (ppm)	Ta (ppm)	Th (ppm)	U (ppm)	V (ppm)	W (ppm)	Zr (ppm)
10x det. limit	1	5	5	5	5	10	5	1	1	1	50	1	5
no samples outside ±25%	2	1	0	1	1		2		1	3		1	1
% within error	83	94	100	94	94		89		92	82		92	94
≥90% data within ±25%		x	x	x	x				x			x	x
samples <10x det. limit						x		x			x		
<90% within ±25%	x						x			x			
Average % relative difference	20	7	6	7	10	N/A	14	N/A	9	12	N/A	21	6
Element	Y (ppm)	La (ppm)	Ce (ppm)	Pr (ppm)	Nd (ppm)	Sm (ppm)	Eu (ppm)	Gd (ppm)	Tb (ppm)	Dy (ppm)	Ho (ppm)	Er (ppm)	Tm (ppm)
10x det. limit	1	5	5	0.2	4	1	0.5	0.5	0.1	0.5	0.5	0.5	0.5
no samples outside ±25%	1	3	3	3	2	2	2	1	2	2	1	1	0
% within error	94	83	83	83	89	89	88	94	89	89	94	94	100
≥90% data within ±25%	x							x			x	x	x
samples <10x det. limit													
<90% within ±25%		x	x	x	x	x	x		x	x			
Average % relative difference	10	19	17	16	15	11	11	12	10	10	11	9	9
Element	Yb (ppm)	Lu (ppm)											
10x det. limit	0.5	0.1											
no samples outside ±25%	0	0											
% within error	100	100											
≥90% data within ±25%	x	x											
samples <10x det. limit													
<90% within ±25%													
Average % relative difference	8	7											
Collahuasi (2006-07) 4BWR Duplicates - Summary													
28 Total no. of elements evaluated													
14 Total no. of elements meeting QC criteria^A													
14 ≥90% duplicates within ±25% of %relative difference													
11 Total no. of elements not meeting QC criteria^B													
11 <90% duplicates within ±25% of %relative difference													
3 Total no. of elements excluded from QC criteria													
3 >50% of samples below 10x detection limit													
(1) % duplicates with ≥90% samples within ±25% of relative difference ((A/(A+B))x100)													50%
(2) Average of average % relative difference:													11%

Table 22: 1FMS

Element	Mo (ppm)	Cu (ppm)	Pb (ppm)	Zn (ppm)	Ag (ppb)	Ni (ppm)	Co (ppm)	Mn (ppm)	As (ppm)	Au (ppb)	Cd (ppm)	Sb (ppm)	Bi (ppm)
10x det. limit	0.1	0.1	0.1	1	20	1	1	10	1	2	0.1	0.2	0.2
no samples outside ±25%	6	10	12	8	5		3	4	6				
% within error	67	44	33	56	58		73	78	63				
≥90% data within ±25%													
samples <10x det. limit						x				x	x	x	x
<90% within ±25%	x	x	x	x	x		x	x	x				
Average % relative difference	21	40	44	42	40	N/A	22	15	23	N/A	N/A	N/A	N/A
Element	Cr (ppm)	B (ppm)	Tl (ppm)	Hg (ppb)	Se (ppm)	Te (ppm)	Ge (ppm)	In (ppm)	Re (ppb)	Be (ppm)	Li (ppm)	Pd (ppb)	Pt (ppb)
10x det. limit	5	10	0.2	50	1	0.2	1	0.2	10	1	1	100	20
no samples outside ±25%	6											5	
% within error	60											62	
≥90% data within ±25%													
samples <10x det. limit		x	x	x	x	x	x	x	x	x		x	x
<90% within ±25%	x										x		
Average % relative difference	37	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	34	N/A	N/A

Collahuasi (2006-07) 1FMS Duplicates - Summary	
26	Total no. of elements evaluated
0	Total no. of elements meeting QC criteria^A
0	≥90% duplicates within ±25% of %relative difference
10	Total no. of elements not meeting QC criteria^B
10	<90% duplicates within ±25% of %relative difference
16	Total no. of elements excluded from QC criteria
16	>50% of samples below 10x detection limit
(1) % duplicates with ≥90% samples within ±25% of relative difference ((A/(A+B))x100)	0%
(2) Average of average % relative difference:	32%

Table 23: 4ALO

Element	LOI (%)
10x det. limit	1
no samples outside ±25%	
% within error	
≥90% data within ±25%	
samples <10x det. limit	x
<90% within ±25%	
Average % relative difference	

Collahuasi (2006-07) LOI Duplicates - Summary	
1	Total no. of elements evaluated
0	Total no. of elements meeting QC criteria ^A
0	≥90% duplicates within ±25% of %relative difference
0	Total no. of elements not meeting QC criteria ^B
0	<90% duplicates within ±25% of %relative difference
1	Total no. of elements excluded from QC criteria
1	>50% of samples below 10x detection limit
(1) % duplicates with ≥90% samples within ±25% of relative difference ((A/(A+B))x100)	N/A
(2) Average of average % relative difference:	N/A

Table 24: 7TDA

Element	Ni (ppm)
10x det. limit	100
no samples outside ±25%	
% within error	
≥90% data within ±25%	
samples <10x det. limit	x
<90% within ±25%	
Average % relative difference	

Collahuasi (2006-07) 7TDA Duplicates - Summary	
1	Total no. of elements evaluated
0	Total no. of elements meeting QC criteria ^A
0	≥90% duplicates within ±25% of %relative difference
0	Total no. of elements not meeting QC criteria ^B
0	<90% duplicates within ±25% of %relative difference
1	Total no. of elements excluded from QC criteria
1	>50% of samples below 10x detection limit
(1) % duplicates with ≥90% samples within ±25% of relative difference ((A/(A+B))x100)	N/A
(2) Average of average % relative difference:	N/A

Table 25: G3B-MS

Element	Au (ppb)	Pt (ppb)	Pd (ppb)
10x det. limit	10	1	5
no samples outside ±25%			
% within error			
≥90% data within ±25%			
samples <10x det. limit	x	x	x
<90% within ±25%			
Average % relative difference			

Collahuasi (2006-07) G3B-MS Duplicates - Summary	
3	Total no. of elements evaluated
0	Total no. of elements meeting QC criteria ^A
0	≥90% duplicates within ±25% of %relative difference
0	Total no. of elements not meeting QC criteria ^B
0	<90% duplicates within ±25% of %relative difference
3	Total no. of elements excluded from QC criteria
3	>50% of samples below 10x detection limit
(1) % duplicates with ≥90% samples within ±25% of relative difference ((A/(A+B))x100)	N/A
(2) Average of average % relative difference:	N/A

Table 26: 4ALC

Element	TOT/C (%)	TOT/S (%)
10x det. limit	0.1	0.1
no samples outside ±25%		
% within error		
≥90% data within ±25%		
samples <10x det. limit	x	x
<90% within ±25%		
Average % relative difference		

Collahuasi (2006-07) 4ALC Duplicates - Summary	
2	Total no. of elements evaluated
0	Total no. of elements meeting QC criteria ^A
0	≥90% duplicates within ±25% of %relative difference
0	Total no. of elements not meeting QC criteria ^B
0	<90% duplicates within ±25% of %relative difference
2	Total no. of elements excluded from QC criteria
2	>50% of samples below 10x detection limit
(1) % duplicates with ≥90% samples within ±25% of relative difference ((A/(A+B))x100)	N/A
(2) Average of average % relative difference:	N/A

QUALITY ASSURANCE/ QUALITY CONTROL OF SOILS GEOCHEMICAL DATA

PROJECT GC51: GEOCHEMICAL BASELINES – COLLAHUASI

**Aisha Gloudon
(PhD student)**

April 2011

**Imperial College Supervisors:
Professor Jane Plant
Dr Nick Voulvoulis**

**AAplc Supervisors:
Dr Christopher Oates**

Centre for Environmental Policy

Executive Summary

Soil samples were collected from the Collahuasi region in two campaigns, the first in 2003-04 and the second in 2006-07 (Table 1). The QA/QC assessment of the soil data shows the dataset is of a high quality.

Table 1: The number of samples analysed in each campaign

Campaign	Total samples	Samples	Field duplicates	S4 standards
2003-04	303	253	25 (10%)	25 (10%)
2006-07	628	572	27 (5%)	29 (5%)

Standards

The accuracy of the data was assessed by analysing S4 standards (internal reference material (IRM)). A pass-fail criterion was established whereby an element passed if ≥ 3 analysed standard samples for each element were outside $\pm 25\%$ of the mean for that standard.

For soils collected at Collahuasi during 2003-04, all of the 44 elements evaluated met the criteria - 100% (Table). For soils collected at Collahuasi during 2006-07, 41 of the 44 elements evaluated met the criteria - 93% (Table 3). Cadmium, Selenium and Antimony failed the criteria.

Table 2: Collahuasi Soils (2003-04) S4 Standards

Table 3: Collahuasi Soils (2006-07) S4 Standards

Collahuasi (2003-04) S4 Standards - Summary		Collahuasi (2006-07) S4 Standards - Summary	
53	Total no. of elements evaluated	53	Total no. of elements evaluated
44	Total no. of elements meeting QC criterion ^A	41	Total no. of elements meeting QC criterion ^A
8	Elements within 2 std dev of mean	1	Elements within 2 std dev of mean
14	Elements within 3 std dev of mean	4	Elements within 3 std dev of mean
40	Elements within $\pm 25\%$ of mean	31	Elements within $\pm 25\%$ of mean
44	Elements with ≤ 3 points outside $\pm 25\%$ of mean	5	Elements with ≤ 3 points outside $\pm 25\%$ of mean
0	Total no. of elements not meeting QC criterion ^B	3	Total no. of elements not meeting QC criterion ^B
0	Elements with ≥ 4 points outside $\pm 25\%$ of mean	3	Elements with ≥ 4 points outside $\pm 25\%$ of mean
9	Total no. of elements excluded from QC criterion	9	Total no. of elements excluded from QC criterion
9	Elements below detection limit	7	Elements below detection limit
0	Elements too close to detection limit	2	Elements too close to detection limit
0	Elements with no certified values for S4	12	Elements with no certified values for S4 ³
% Elements Meeting Criterion*: <small>*((A/(A+B))x100)</small>		% Elements Meeting Criterion*: 93%	
% Elements within ± 3 std dev and/or $\pm 25\%$ of mean: 91%		% Elements within ± 3 std dev and/or $\pm 25\%$ of mean: 61%	

³Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu

Field Duplicates

Data were evaluated for precision by comparing duplicates against two pass-fail criteria:

- 1) An element passed if 95% of samples were within $\pm 20\%$ of the percentage relative difference
- 2) The entire dataset passed if the average percentage relative difference of all analytes was $\leq \pm 20\%$

For soils collected at Collahuasi during 2003-04, 33 of the 34 elements evaluated met the first criterion, 97%. Overall the average percentage relative difference for analysed elements was 4% demonstrating a high level of precision (Table).

For soils collected at Collahuasi during 2006-07, 5 of the 50 elements evaluated met the first criterion, 10%. Overall, the average percentage relative difference for analysed elements was 14%, demonstrating a high level of precision (Table).

Table 4: Collahuasi Soils (2003-04) Field Duplicates
Table 5: Collahuasi Soils (2006-07) Field Duplicates

Collahuasi (2003-04) Duplicates - Summary	
53	Total no. of elements evaluated
33	Total no. of elements meeting first QC criterion ^A
33	≥95% duplicates within ±20% of %relative difference
1	Total no. of elements not meeting first QC criterion ^B
1	<95% duplicates within ±20% of %relative difference
19	Total no. of elements excluded from QC criterion
19	>50% of samples below 10x detection limit
(1) % duplicates with ≥95% samples within ±20% of relative difference $((A/(A+B)) \times 100)$	97%
(2) Average of average % relative difference:	4%

Collahuasi (2006-07) Duplicates - Summary	
65	Total no. of elements evaluated
5	Total no. of elements meeting QC criterion ^A
5	≥95% dupli cates within ±20% of %relative difference
45	Total no. of elements not meeting QC criterion ^B
45	<95% dupli cates within ±20% of %relative difference
15	Total no. of elements excluded from QC criterion
15	>50% of samples below 10x detection limit
(1) % duplicates with ≥95% samples within ±20% of relative difference $((A/(A+B)) \times 100)$	10%
(2) Average of average % relative difference:	14%

Summary of QA/QC Results

Soil samples were collected from the Collahuasi region in two campaigns, the first in 2003-04 and the second in 2006-07 (Table 1).

Table 1: The number of samples analysed in each campaign

Campaign	Total samples	Samples	Field duplicates	S4 standards
2003-04	303	253	25 (10%)	25 (10%)
2006-07	628	572	27 (5%)	29 (5%)

The QA/QC assessment of the soil data shows a high quality dataset.

Standards

In order to evaluate the analytical accuracy of the group 1F-MS method, S4 standards (internal reference material (IRM)) were inserted into each analytical run and the results compared against known performance gates using graphs. Performance gates for this analytical method were referenced for 53 elements. Performance gates included:

- 1) the mean of the S4 IRM
- 2) ±25% of the mean
- 3) ±2 standard deviation of the mean
- 4) ±3 standard deviation of the mean

Ideally, 95% of all samples should fall between ±2 standard deviations (warning lines), with 99% between ±3 standard deviations (failure lines). The standard suggests that a batch of analyses has failed if one or more samples fall outside the failure lines or more than two standards fall outside any warning line.

To allow for the intrinsic heterogeneity of soil samples, sieved at 250 µm, an additional pass-fail criterion was established. An element passed if 3 analysed standard samples for each element were outside ±25% of the mean for that standard. Elements below or too close to their detection limit were excluded from evaluation.

Graphs for these standards show the analytical results for the internal reference material (IRM) plotted against the analytical order (Figure 1).

For soils collected at Collahuasi during 2003-04, the majority of elements had <±10% bias between their mean and the certified S4 mean. In addition, all 44 elements evaluated, satisfied the criterion, 100%. Overall the level of accuracy for the dataset is high (Table 6).

For soils collected at Collahuasi during 2006-07, the majority of elements had <±10% bias between their mean and the certified S4 mean. In addition, 41 of the 44 evaluated elements satisfied the criterion, 93%. Cadmium, Selenium and Antimony failed. Overall the dataset demonstrates a high level of accuracy (Table 7).

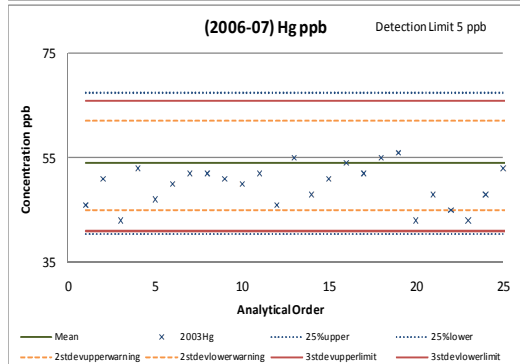
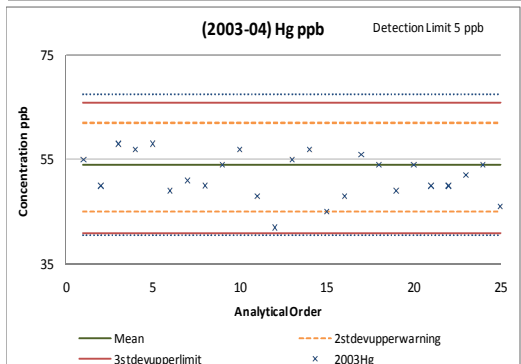
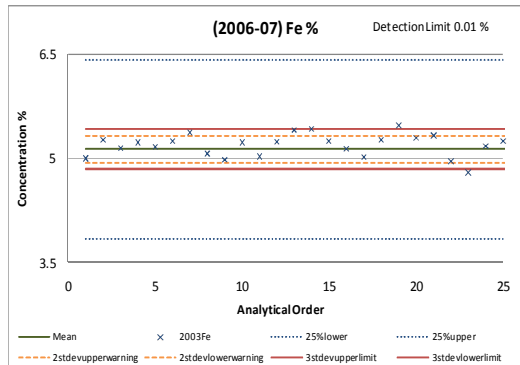
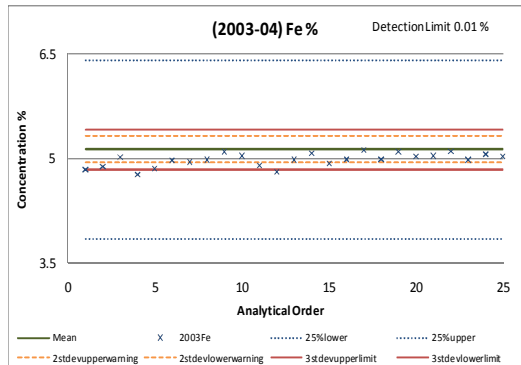
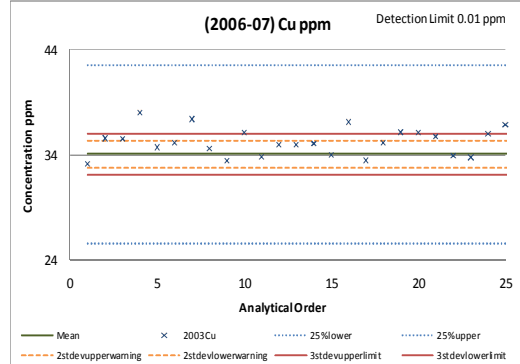
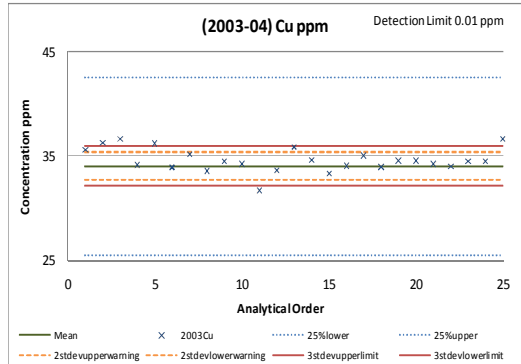
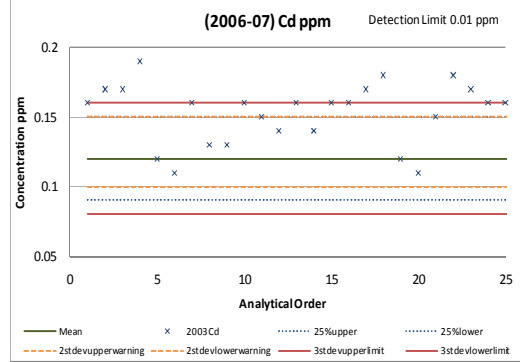
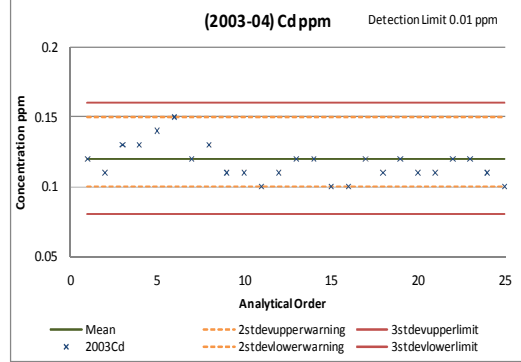
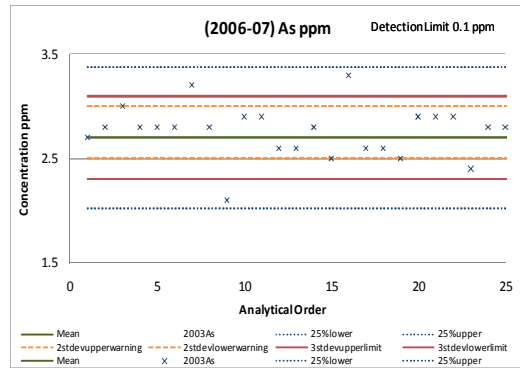
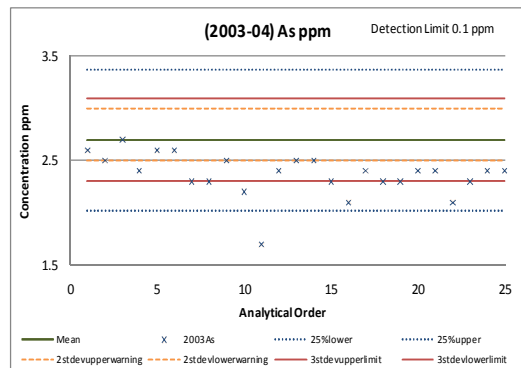


Figure 1: As, Cd, Cu, Fe, Hg, K, Mo, Pb, S, Zn Collahuasi soils S4 IRM. Green line represents the reference mean of the indicated determinant, dashed orange lines = ± 2 std dev., dashed red lines = ± 3 std dev., purple line indicates the detection limit.

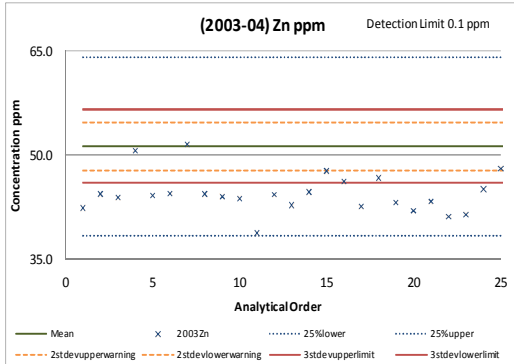
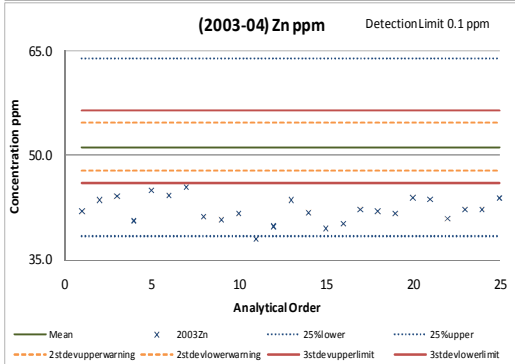
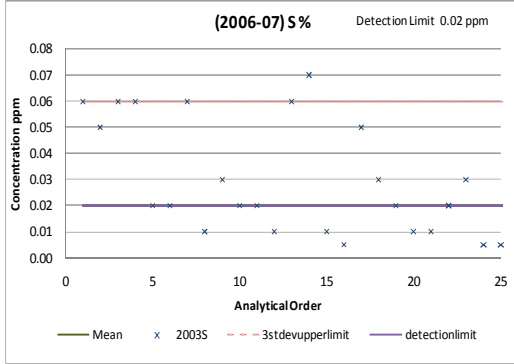
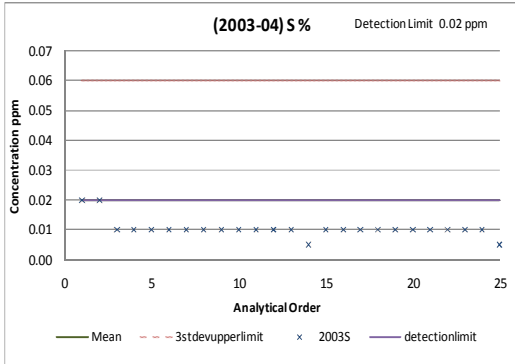
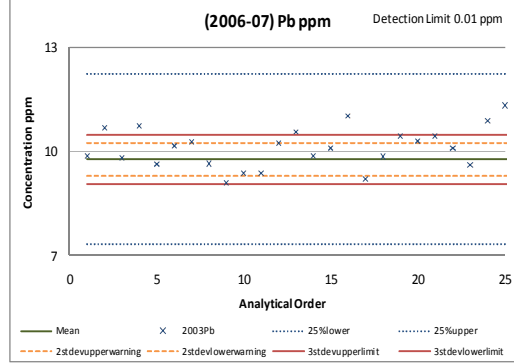
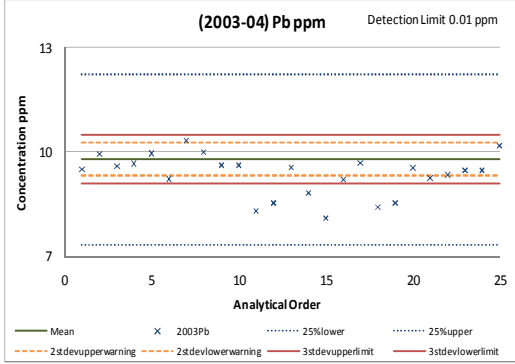
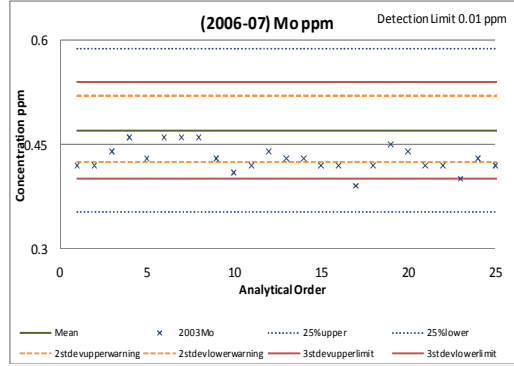
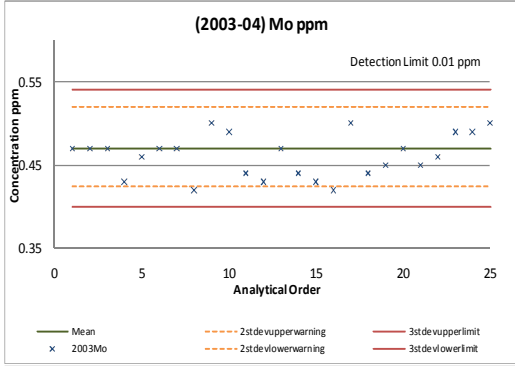
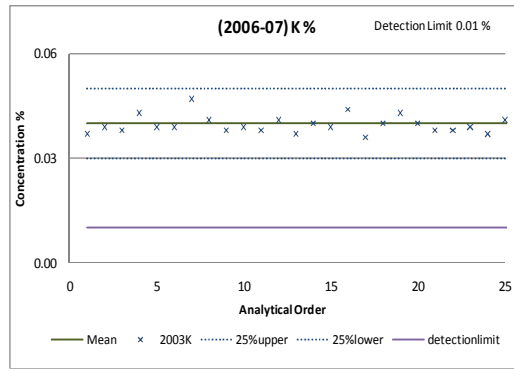
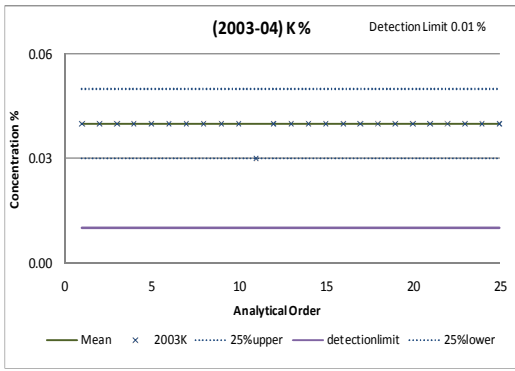


Figure 1: As, Cd, Cu, Fe, Hg, K, Mo, Pb, S, Zn Collahuasi soils S4 IRM. Green line represents the reference mean of the IRM of the indicated determinant, dashed orange lines = ± 2 std dev., dashed red lines = ± 3 std dev., purple line indicates the detection limit.

Table 6: (2003-04 Collahuasi Soils) Accuracy assessment for the S4 IRM

Element	Ag_ppb	Al_per	As_ppm	Au_ppb	B_ppm	Ba_ppm	Be_ppm	Bi_ppm	Ca_per	Cd_ppm	Ce_ppm	Co_ppm	Cr_ppm
Within 2 std dev				x			x	x		x			
Within 3 std dev													
Within ±25% of mean		x				x			x		x	x	x
≤3 outside ±25% of mean	x		x										
Outside Limits													
Evaluation					below det.								
mean S4 data	70	6.45	2.4	1.3	1	87.5	0.9	0.17	0.48	0.12	44.9	14.8	53.9
mean S4 certified	67	5.79	2.7	0.9	1	92.0	1.0	0.18	0.50	0.12	43.5	15.3	55.2
Bias ¹	0.04	0.11	-0.11	0.44		-0.05	-0.10	-0.06	-0.04	0.00	0.03	-0.03	-0.02
% Bias ²	4.48	11.40	-11.11	44.44		-4.89	-10.00	-5.56	-4.00	0.00	3.22	-3.27	-2.36
mean of data	314	1.58	39.9	7.8	8	199.6	0.9	0.69	0.30	0.90	34.0	11.2	14.7
detection limit	2	0.01	0.1	0.2	1	0.5	0.1	0.02	0.01	0.01	0.1	0.1	0.5
10x detection limit	20	0.10	1.0	2.0	10.00	5.00	1.00	0.20	0.10	0.10	1.00	1.0	5.00
Element	Cs_ppm	Cu_ppm	Fe_per	Ga_ppm	Ge_ppm	Hf_ppm	Hg_ppb	In_ppm	K_per	La_ppm	Li_ppm	Mg_per	Mn_ppm
Within 2 std dev									x				
Within 3 std dev							x					x	
Within ±25% of mean	x	x	x	x		x				x	x		x
≤3 outside ±25% of mean								x					
Outside Limits													
Evaluation					below det.								
mean S4 data	1.28	34.62	4.98	13.3	0.10	1.21	52	0.07	0.04	14.9	7.8	0.50	520
mean S4 certified	1.30	34.06	5.13	13.9	0.10	1.25	54	0.07	0.04	14.7	8.3	0.52	559
Bias ¹	-0.02	0.02	-0.03	-0.04		-0.03	-0.04	0.00	0.00	0.01	-0.06	-0.04	-0.07
% Bias ²	-1.54	1.64	-2.92	-4.32		-3.20	-3.70	0.00	0.00	1.36	-6.02	-3.85	-6.98
mean of data	4.85	127.00	2.96	5.0	0.07	0.22	28	0.13	0.21	17.6	21.8	0.47	1016
detection limit	0.02	0.01	0.01	0.1	0.1	0.02	5	0.02	0.01	0.5	0.1	0.01	1
10x detection limit	0.20	0.10	0.10	1.00	1	0.20	50.00	0.20	0.10	5.00	1.00	0.10	10
Element	Mo_ppm	Na_per	Nb_ppm	Ni_ppm	P_per	Pb_ppm	Pd_ppb	Pt_ppb	Rb_ppm	Re_ppb	S_per	Sb_ppm	Sc_ppm
Within 2 std dev				x									
Within 3 std dev	x		x									x	
Within ±25% of mean		x			x	x			x				x
≤3 outside ±25% of mean													
Outside Limits													
Evaluation					below det.		below det.	below det.		below det.	below det.		
mean S4 data	0.46	0.131	0.69	10.3	0.049	9.35	5	1	3.5	1	0.01	0.09	14.1
mean S4 certified	0.47	0.136	0.67	10.4	0.052	9.78	10	2	3.6	1	0.02	0.09	14.7
Bias ¹	-0.02	-0.04	0.03	-0.01	-0.06	-0.04			-0.03			0.00	-0.04
% Bias ²	-2.13	-3.68	2.99	-0.96	-5.77	-4.40			-2.78			0.00	-4.08
mean of data	3.70	0.021	0.22	11.7	0.060	57.92	5	1	21.0	1	0.05	2.01	4.2
detection limit	0.01	0.001	0.02	0.1	0.001	0.01	10	2	0.1	1	0.02	0.02	0.1
10x detection limit	0.10	0.01	0.20	1.0	0.01	0.10	100.00	20.00	1.00	10.00	0.20	0.20	1.00
Element	Se_ppm	Sn_ppm	Sr_ppm	Ta_ppm	Te_ppm	Th_ppm	Ti_per	Tl_ppm	U_ppm	V_ppm	W_ppm	Y_ppm	Zn_ppm
Within 2 std dev			x				x						
Within 3 std dev	x												
Within ±25% of mean		x					x	x	x	x		x	
≤3 outside ±25% of mean													x
Outside Limits													
Evaluation				below det.	below det.						below det.		
mean S4 data	0.49	1.3	47.1	0.03	0.01	2.8	0.486	0.21	0.7	181	0.1	19.78	42.2
mean S4 certified	0.54	1.3	45.5	0.05	0.02	2.7	0.475	0.20	0.7	176	0.1	20.31	51.2
Bias ¹	-0.1	0.00	0.03			0.04	0.02	0.03	0.00	0.03		-0.03	-0.18
% Bias ²	-10.0	0.00	3.49			3.70	2.32	2.60	0.00	2.84		-2.61	-17.58
mean of data		0.8	73.25	0.03	0.14	7.0	0.071	0.23	1.4	67.24	0.5	10.31	178.9
detection limit	0.1	0.1	0.50	0.05	0.02	0.1	0.001	0.02	0.1	2.00	0.1	0.01	0.1
10x detection limit	1.0	1.00	5.00	0.50	0.20	1.0	0.01	0.20	1.0	20.00	1.00	0.10	1.0
Element	Zr_ppm												
Within 2 std dev													
Within 3 std dev													
Within ±25% of mean	x												
≤3 outside ±25% of mean													
Outside Limits													
Evaluation													
mean S4 data	70.5												
mean S4 certified	66.4												
Bias ¹	0.06												
% Bias ²	6.17												
mean of data	9.3												
detection limit	0.1												
10x detection limit	1.00												

	>10%
	5 to 10%
	2 to 5%
	-2 to 2%
	-2 to -5%
	-5 to -10%
	<-10%

¹ bias = ((x data - x standard)/x standard)
² % bias = bias *100

Table 7: (2006-07 Collahuasi Soils) Accuracy assessment for the S4 IRM

Element	Ag_ppb	Al_per	As_ppm	Au_ppb	B_ppm	Ba_ppm	Be_ppm	Bi_ppm	Ca_per	Cd_ppm	Ce_ppm	Co_ppm	Cr_ppm
Within 2 std dev				x									
Within 3 std dev							x						
Within ±25%		x	x			x		x	x		x	x	x
≤3 outside ±25%	x												
Outside Limits										x			
Evaluation					below det.					7 outside > ±25%†			
mean S4 data	71	6.26	2.8	1.1	1	90	0.9	0.20	0.51	0.15	40.6	15.7	52.4
mean S4 certified	67	5.79	2.7	0.9	1	92	1.0	0.18	0.50	0.12	43.5	15.3	55.2
Bias ¹	0	0.08	0.0	0.2	N/A	-0.02	-0.07	0.09	0.02	0.26	-0.07	0.03	-0.05
% Bias ²	6	8.06	2.6	20.7	N/A	-2	-6.90	9.20	2.05	26.15	-6.78	2.57	-5.08
mean of data	444	1.72	56.2	9.5	8	212	0.8	0.83	0.24	0.90	25.3	10.1	14.8
median of data	168	1.69	35.2	2.9	8	193	0.7	0.50	0.22	0.54	23.4	9.4	14.4
detection limit	2	0.01	0.1	0.2	1	1	0.1	0.02	0.01	0.01	0.1	0.1	0.5
10x detection limit	20	0.10	1.0	2.0	10	5	1.00	0.20	0.10	0.10	1.00	1.0	5.00
Element	Cs_ppm	Cu_ppm	Fe_per	Ga_ppm	Ge_ppm	Hf_ppm	Hg_ppb	In_ppm	K_per	La_ppm	Li_ppm	Mg_per	Mn_ppm
Within 2 std dev													
Within 3 std dev							x	x			x		
Within ±25%	x	x	x	x		x			x	x		x	x
≤3 outside ±25%													
Outside Limits													
Evaluation					below det.								
mean S4 data	1.31	35.28	5.18	13.5	0.12	1.29	50	0.07	0.04	15.56	7.8	0.50	503
mean S4 certified	1.30	34.06	5.13	13.9	0.10	1.25	54	0.07	0.04	14.7	8.3	0.52	559
Bias ¹	0.01	0.04	0.01	-0.03	N/A	0.03	-0.07	0.06	-0.01	0.06	-0.06	-0.04	-0.10
% Bias ²	1.01	3.60	1.01	-2.75	N/A	3.14	-7.22	5.91	-0.60	5.84	-6.11	-3.65	-9.96
mean of data	4.54	178.00	3.00	5.0	0.07	0.25	25	0.08	0.18	15.2	20.5	0.43	825
median of data	4.42	92.83	2.94	4.9	0.05	0.25	12	0.05	0.18	14.3	20.0	0.42	635
detection limit	0.02	0.01	0.01	0.1	0.1	0.02	5	0.02	0.01	0.5	0.1	0.01	1
10x detection limit	0.20	0.10	0.10	1.00	1	0.20	50.00	0.20	0.10	5.00	1.00	0.10	10
Element	Mo_ppm	Na_per	Nb_ppm	Ni_ppm	P_per	Pb_ppm	Pd_ppb	Pt_ppb	Rb_ppm	Re_ppb	S_per	Sb_ppm	Sc_ppm
Within 2 std dev													
Within 3 std dev													
Within ±25%	x			x	x	x			x				x
≤3 outside ±25%		x	x										
Outside Limits												x	
Evaluation						below det.	below det.		below det.	too close to det. limit		1 outside > ±25%†	
mean S4 data	0.43	0.148	0.69	10.6	0.055	10.12	8	1	3.6	1	0.03	0.10	15.6
mean S4 certified	0.47	0.136	0.67	10.4	0.052	9.78	10	2	3.6	1	0.02	0.09	14.7
Bias ¹	-0.09	0.09	0.03	0.02	0.07	0.04	N/A	N/A	-0.01	N/A	N/A	0.15	0.06
% Bias ²	-8.58	8.57	2.68	1.62	6.63	3.52	N/A	N/A	-0.77	N/A	N/A	15.33	6.31
mean of data	3.04	0.021	0.18	12.2	0.062	56.50	5	1	20.0	1	0.04	2.56	4.2
median of data	2.88	0.020	0.13	11.9	0.058	36.33	5	1	19.5	1	0.04	1.71	4.1
detection limit	0.01	0.001	0.02	0.1	0.001	0.01	10	2	0.1	1	0.02	0.02	0.1
10x detection limit	0.10	0.01	0.20	1.0	0.01	0.10	100.00	20.00	1.00	10.00	0.20	0.20	1.00
Element	Se_ppm	Sn_ppm	Sr_ppm	Ta_ppm	Te_ppm	Th_ppm	Tl_per	Tl_ppm	U_ppm	V_ppm	W_ppm	Y_ppm	Zn_ppm
Within 2 std dev													
Within 3 std dev													
Within ±25%		x	x				x	x		x		x	x
≤3 outside ±25%						x			x				
Outside Limits	x												
Evaluation	4 outside > ±25%†			below det.	too close to det. limit						below det.		
mean S4 data	0.6	1.3	48.2	0.03	0.05	3.1	0.479	0.23	0.8	168	0.1	19.63	44.7
mean S4 certified	0.5	1.3	45.5	0.05	0.02	2.7	0.475	0.20	0.7	176	0.1	20.31	51.2
Bias ¹	0.08	0.00	0.06	N/A	N/A	0.13	0.01	0.16	0.18	-0.04	N/A	-0.03	-0.13
% Bias ²	7.64	-0.21	6.03	N/A	N/A	13.28	0.93	15.86	18.37	-4.43	N/A	-3.32	-12.65
mean of data	0.4	1.0	85.73	0.03	0.19	6.1	0.071	0.27	1.3	59.54	1.0	7.54	186.8
median of data	0.4	0.8	85.25	0.03	0.12	5.9	0.067	0.25	1.2	58.00	0.4	6.64	117.7
detection limit	0.1	0.1	0.50	0.05	0.02	0.1	0.001	0.02	0.1	2.00	0.1	0.01	0.1
10x detection limit	1.00	1.00	5.00	0.50	0.20	1.0	0.01	0.20	1.0	20.00	1.00	0.10	1.0
Element	Zr_ppm												
Within 2 std dev													
Within 3 std dev													
Within ±25%	x												
≤3 outside ±25%													
Outside Limits													
Evaluation													
mean S4 data	73.4												
mean S4 certified	66.4												
Bias ¹	0.11												
% Bias ²	10.59												
mean of data	10.0												
median of data	10.3												
detection limit	0.1												
10x detection limit	1.00												

Red	>10%
Orange	5 to 10%
Green	2 to 5%
Light Green	-2 to 2%
Light Blue	-2 to -5%
Yellow	-5 to -10%
Dark Blue	<-10%

where the initial 2s and 3s parameter are > +/-25%
¹ likely to be an anomaly
¹ bias = ((x data - x standard)/x standard)
² % bias = bias *100
³ Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu

Field Duplicates

During the 2003-04 and 2006-07 campaigns, field duplicates were collected to determine the sampling variation (Table 1).

The duplicate results are presented as graphs for each chemical element, comparing the percentage relative difference plotted against the original-duplicate mean (1).

$$y\text{-axis: } 100 * \frac{\text{Original} - \text{Duplicate}}{\frac{1}{2}(\text{Original} + \text{Duplicate})} \quad (1)$$

$$x\text{-axis: } \frac{1}{2}(\text{Original} + \text{Duplicate})$$

In order to evaluate the precision of the data collected, the percentage relative difference between duplicates was calculated. Two pass-fail criteria were applied to each element;

- 1) An element passed where 95% of values fell within $\pm 20\%$ of the percentage relative difference
- 2) The entire dataset passed if the average percentage relative difference of all analytes was $< \pm 20\%$ *

A black solid line which represents ten times the detection limit is plotted parallel to Y axis (Figure 2). Samples less than 10 times the detection limit and elements where more than 50% of samples were less than 10 times the detection limit were excluded from evaluation.

*Elements with sample concentrations close to detection limits show increased variability resulting from difficulties maintaining accuracy of measurements at these concentrations. The second pass-fail criterion accounts for this variability by considering the overall average percentage relative difference per element and reflects the overall behaviour of the dataset.

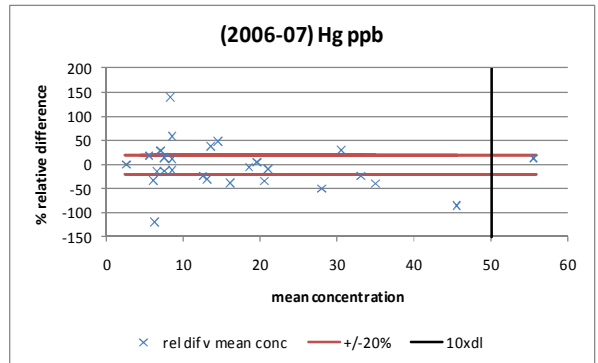
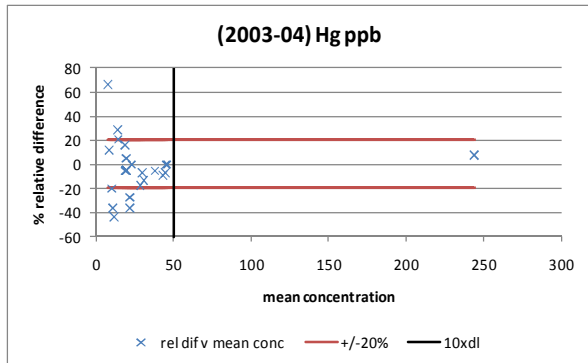
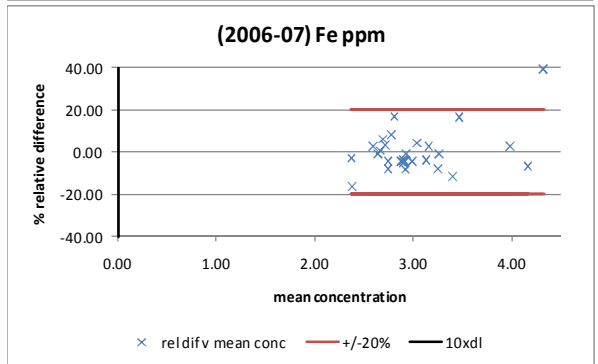
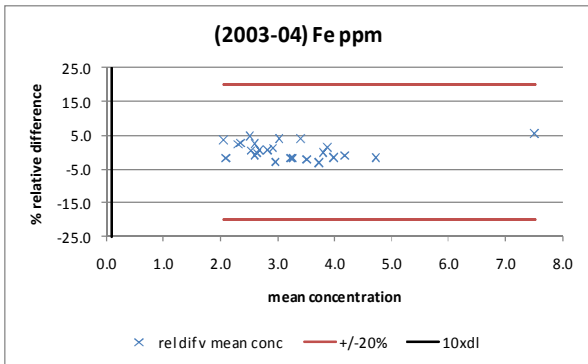
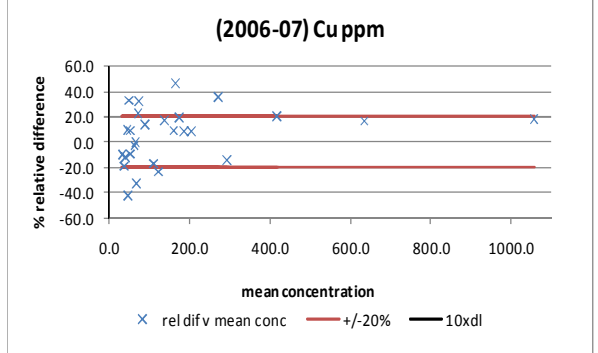
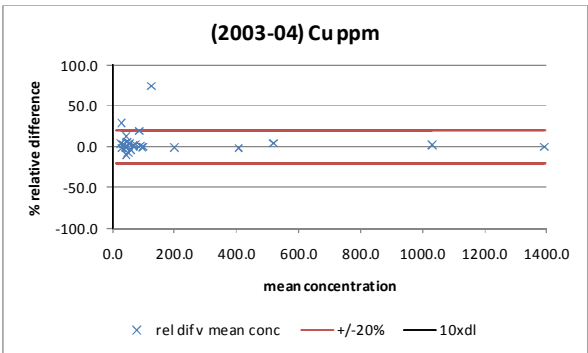
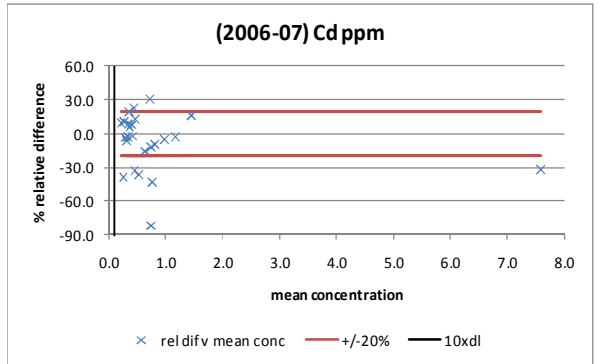
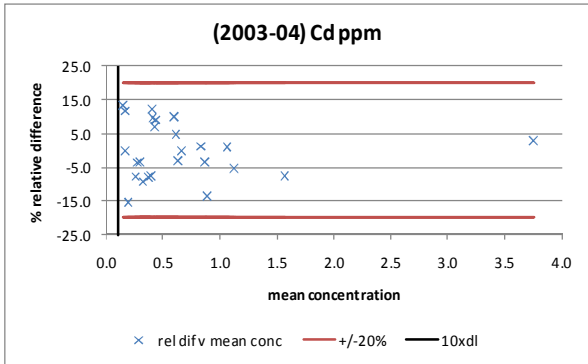
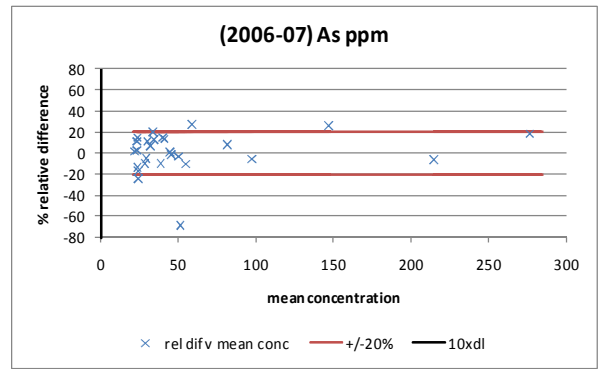
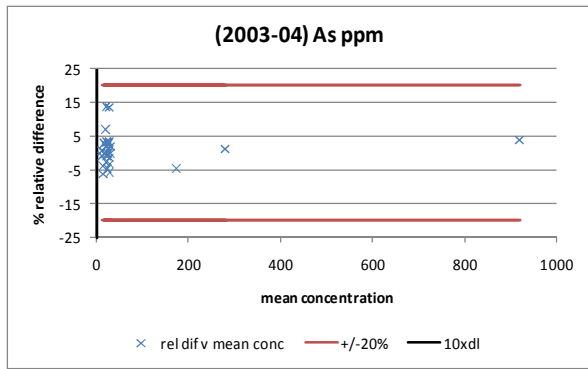


Figure 1: As, Cd, Cu, Fe, Hg, K, Mo, Pb, S, Zn duplicate graphs. LH column = 2003-04 soils, RH column = 2006-07 soils. 9
 Horizontal red lines represent $\pm 20\%$ error margins. Vertical black lines represent ten times the lower detection limit.

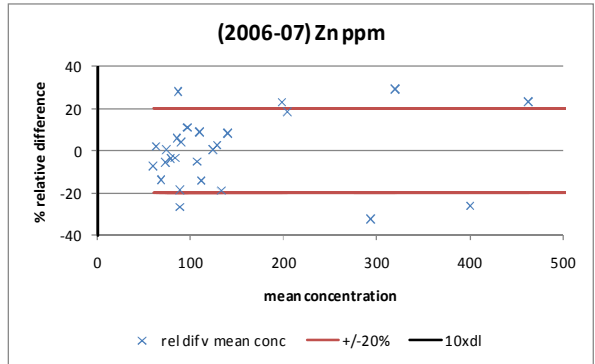
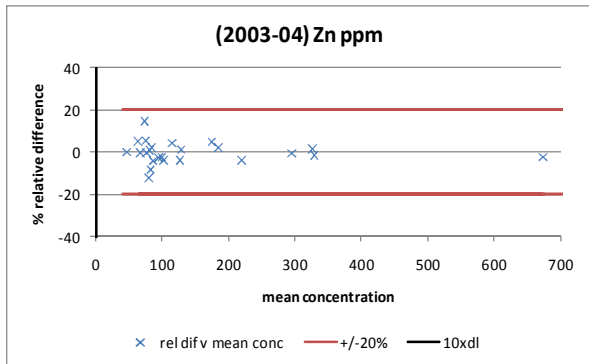
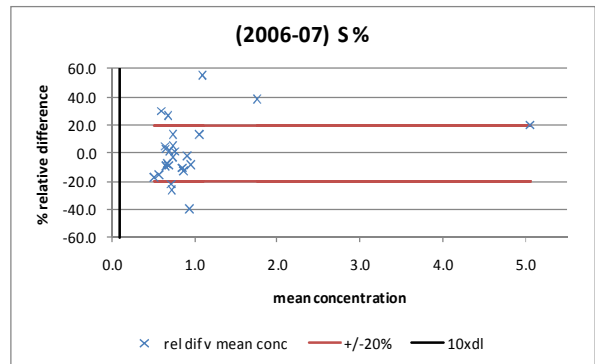
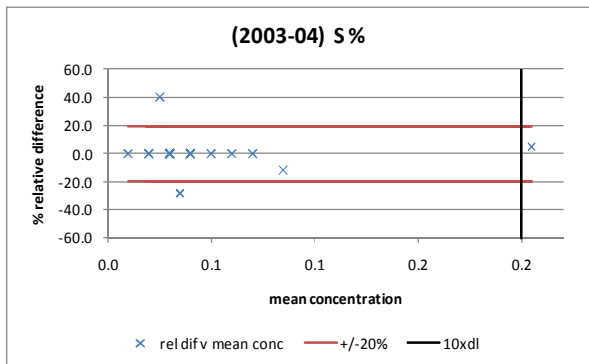
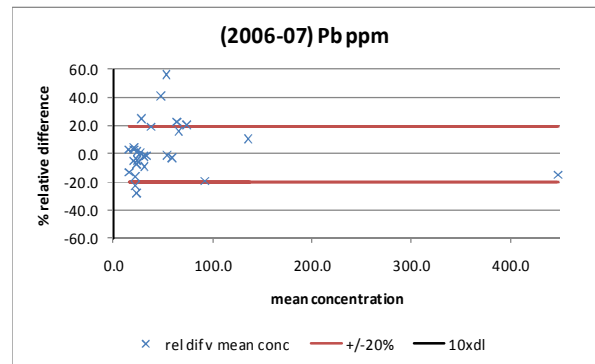
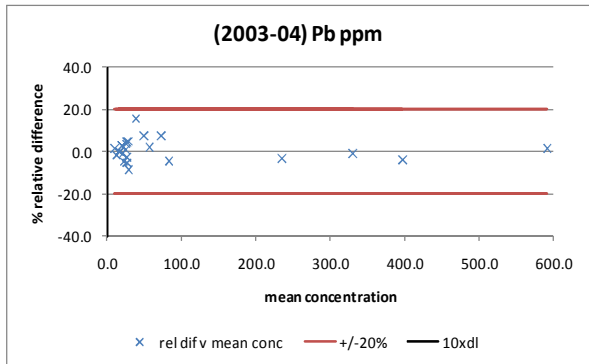
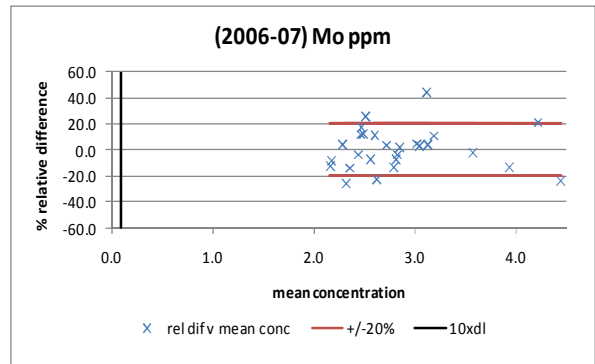
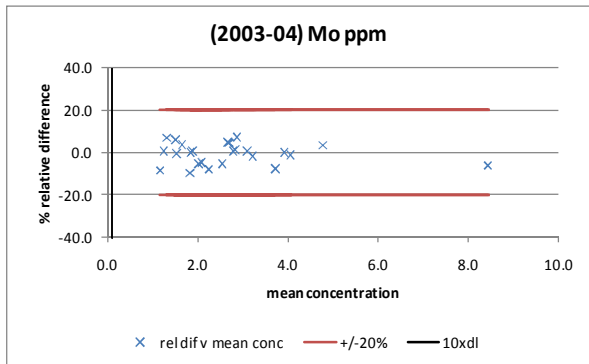
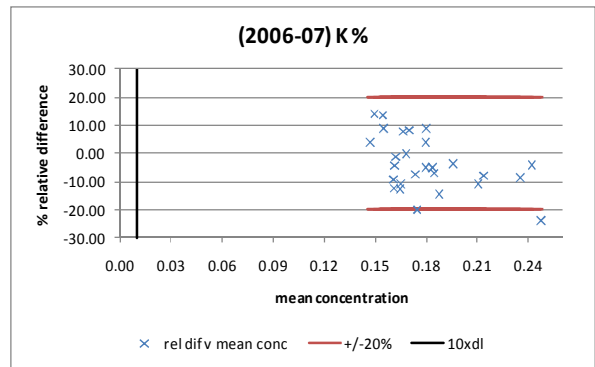
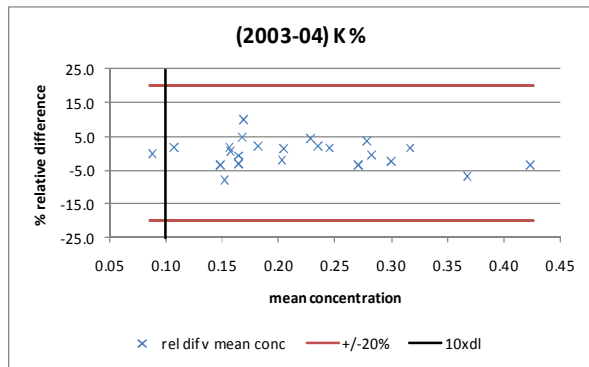


Figure 1: As, Cd, Cu, Fe, Hg, K, Mo, Pb, S, Zn duplicate graphs. LH column = 2003-04 soils, RH column = 2006-07 soils. Horizontal red lines represent $\pm 20\%$ error margins. Vertical black lines represent ten times the lower detection limit.

For soils collected at Collahuasi during 2003-04, 33 of the 34 elements evaluated fell within $\pm 20\%$ of the percentage relative difference, 97%. Overall, the average percentage relative difference for all elements analysed was 4% demonstrating a high level of precision.

Table 8: (Collahuasi Soils 2003-04) Reproducibility assessment for field duplicates

Element	Ag_ppb	Al_per	As_ppm	Au_ppb	B_ppm	Ba_ppm	Be_ppm	Bi_ppm	Ca_per	Cd_ppm	Ce_ppm	Co_ppm	Cr_ppm
10x detection limit	20.00	0.1	1.00	2.00	10	5	1	0.2	0.1	0.1	1	1.00	5
no samples outside $\pm 20\%$	0	0	0			0		1	0	0	0	0	0
% within error	100	100	100			100		96	100	100	100	100	100
$\geq 95\%$ data within $\pm 20\%$	x	x	x			x		x	x	x	x	x	x
samples <10x det. limit				x	x		x						
<95% within $\pm 20\%$													
Average % relative difference > $\pm 20\%$	5	3	4	N/A	N/A	5	N/A	6	3	7	5	3	3
Element	Cs_ppm	Cu_ppm	Fe_per	Ga_ppm	Ge_ppm	Hf_ppm	Hg_ppb	In_ppm	K_per	La_ppm	Li_ppm	Mg_per	Mn_ppm
10x detection limit	0.2	0.10	0.10	1	1	0.2	50	0.2	0.1	5	1	0.1	10.00
no samples outside $\pm 20\%$	0	2	0	0					0	0	0	0	0
% within error	100	92	100	100					100	100	100	100	100
$\geq 95\%$ data within $\pm 20\%$	x		x	x					x	x	x	x	x
samples <10x det. limit					x	x	x	x					
<95% within $\pm 20\%$		x											
Average % relative difference > $\pm 20\%$	4	8	2	4	N/A	N/A	N/A	N/A	3	5	5	2	3
Element	Mo_ppm	Na_per	Nb_ppm	Ni_ppm	P_per	Pb_ppm	Pd_ppb	Pt_ppb	Rb_ppm	Re_ppb	S_per	Sb_ppm	Sc_ppm
10x detection limit	0.10	0.01	0.2	1.00	0.01	0.10	100	20	1	10	0.2	0.2	1
no samples outside $\pm 20\%$	0	0		0	0	0			0			1	0
% within error	100	100		100	100	100			100			96	100
$\geq 95\%$ data within $\pm 20\%$	x	x		x	x	x			x			x	x
samples <10x det. limit			x				x	x		x	x		
<95% within $\pm 20\%$													
Average % relative difference > $\pm 20\%$	4	4	N/A	4	3	4	N/A	N/A	4	N/A	N/A	6	3
Element	Se_ppm	Sn_ppm	Sr_ppm	Ta_ppm	Th_ppm	Ti_per	Tl_ppm	U_ppm	Te_ppm	W_ppm	V_ppm	Y_ppm	Zn_ppm
10x detection limit	1	1	5	0.5	1.00	0.01	0.2	1.00	0.2	1	20	0.1	1.00
no samples outside $\pm 20\%$			0		0	0					0	0	0
% within error			100		100	100					100	100	100
$\geq 95\%$ data within $\pm 20\%$			x		x	x					x	x	x
samples <10x det. limit	x	x		x			x	x	x	x			
<95% within $\pm 20\%$													
Average % relative difference > $\pm 20\%$	N/A	N/A	2	N/A	4	4	N/A	N/A	N/A	N/A	2	3	4
Element	Zr_ppm												
10x detection limit	1												
no samples outside $\pm 20\%$	0												
% within error	100												
$\geq 95\%$ data within $\pm 20\%$	x												
samples <10x det. limit													
<95% within $\pm 20\%$													
Average % relative difference > $\pm 20\%$	4												

Collahuasi (2003-04) Duplicates - Summary	
53	Total no. of elements evaluated
33	Total no. of elements meeting first QC criterion ^A
33	$\geq 95\%$ duplicates within $\pm 20\%$ of %relative difference
1	Total no. of elements not meeting first QC criterion ^B
1	<95% duplicates within $\pm 20\%$ of %relative difference
19	Total no. of elements excluded from QC criterion
19	>50% of samples below 10x detection limit
(1) % duplicates with $\geq 95\%$ samples within $\pm 20\%$ of relative difference $\frac{(A/(A+B)) \times 100}{}$	97%
(2) Average of average % relative difference:	4%

For soils collected at Collahuasi during 2006-07, only 5 of the 50 elements evaluated fell within $\pm 20\%$ of percentage relative difference, 10%. However, the dataset satisfied the second criteria, with an average percentage relative difference across the dataset of $< \pm 20\%$.

The elements analysed exhibited more variability than the 2003-04 dataset and this is reflected in the high failure of the first criterion. As reflected in the results of the second criterion however, the range of variability is low consistently $\leq \pm 20\%$ except for Au, which probably reflects the well known nugget effect during sub analysis.

Overall, the average percentage relative difference for all elements analysed was 14%. Hence, the dataset has an acceptable level of precision for further work.

Table 9: (Collahuasi Soils 2006-07) Reproducibility assessment for field duplicates

Element	Ag_ppb	Al_per	As_ppm	Au_ppb	B_ppm	Ba_ppm	Be_ppm	Bi_ppm	Ca_per	Cd_ppm	Ce_ppm	Co_ppm	Cr_ppm
10x detection limit	20.00	0.01	1.00	2.00	10	5	1	0.2	0.01	0.1	1	1.00	5
no samples outside $\pm 20\%$	6	6	3	13		3		6	3	8	3	3	10
% within error	78	78	89	28		89		78	89	70	89	89	63
$\geq 95\%$ data within $\pm 20\%$													
samples <10x det. limit					x		x						
<95% within $\pm 20\%$	x	x	x	x		x		x	x	x	x	x	x
Average % relative difference > $\pm 20\%$	15	14	13	60	N/A	9	N/A	13	11	18	11	10	18
Element	Cs_ppm	Cu_ppm	Dy_ppm	Er_ppm	Eu_ppm	Fe_per	Ga_ppm	Gd_ppm	Ge_ppm	Hf_ppm	Hg_ppb	Ho_ppm	In_ppm
10x detection limit	0.2	0.10	0.2	0.2	0.2	0.01	1	0.2	1	0.2	50	0.2	0.2
no samples outside $\pm 20\%$	7	9	5	3	5	1	7	8				3	7
% within error	74	67	81	80	81	96	74	70				89	74
$\geq 95\%$ data within $\pm 20\%$						x							
samples <10x det. limit									x	x	x		
<95% within $\pm 20\%$	x	x	x	x	x		x	x				x	x
Average % relative difference > $\pm 20\%$	16	19	14	16	15	7	14	16	N/A	N/A	N/A	13	15
Element	K_per	La_ppm	Li_ppm	Lu_ppm	Mg_per	Mn_ppm	Mo_ppm	Na_per	Nb_ppm	Nd_ppm	Ni_ppm	P_per	Pb_ppm
10x detection limit	0.01	5	1	0.2	0.1	10.00	0.10	0.01	0.2	0.2	1.00	0.01	0.10
no samples outside $\pm 20\%$	1	7		2	3	4	6	2		7	4	4	7
% within error	96	74		93	89	85	78	93		74	85	85	74
$\geq 95\%$ data within $\pm 20\%$	x												
samples <10x det. limit			x						x				
<95% within $\pm 20\%$		x		x	x	x	x	x		x	x	x	x
Average % relative difference > $\pm 20\%$	9	16	N/A	11	9	13	12	9	N/A	15	11	11	14
Element	Pd_ppb	Pr_ppm	Pt_ppb	Rb_ppm	Re_ppb	S_per	Sb_ppm	Sc_ppm	Se_ppm	Sm_ppm	Sn_ppm	Sr_ppm	Ta_ppm
10x detection limit	100	0.2	20	1	10	0.1	0.2	1	1	0.2	0.2	5	0.5
no samples outside $\pm 20\%$		5		5		7	6	3		11	8	0	
% within error		81		81		74	78	89		59	70	100	
$\geq 95\%$ data within $\pm 20\%$												x	
samples <10x det. limit	x		x		x				x				x
<95% within $\pm 20\%$		x		x	x	x	x	x		x	x		
Average % relative difference > $\pm 20\%$	N/A	15	N/A	15	N/A	16	14	13	N/A	19	16	9	N/A
Element	Tb_ppm	Te_ppm	Th_ppm	Ti_per	Tl_ppm	Tm_ppm	U_ppm	V_ppm	W_ppm	Y_ppm	Yb_ppm	Zn_ppm	Zr_ppm
10x detection limit	0.1	0.2	1.00	0.01	0.2	0.1	0.10	20	0.1	0.1	0.1	1.00	1
no samples outside $\pm 20\%$	7		3	6	6	5	2	1	1	7		7	
% within error	74		89	78	78	81	93	96	96	74		74	
$\geq 95\%$ data within $\pm 20\%$								x	x				
samples <10x det. limit		x									x		x
<95% within $\pm 20\%$	x		x	x	x	x	x			x		x	
Average % relative difference > $\pm 20\%$	12	N/A	11	16	15	14	9	7	15	15	N/A	13	N/A

Collahuasi (2006-07) Duplicates - Summary

65	Total no. of elements evaluated	
5	Total no. of elements meeting QC criterion ^A	
5	$\geq 95\%$ duplicates within $\pm 20\%$ of %relative difference	
45	Total no. of elements not meeting QC criterion ^B	
45	<95% duplicates within $\pm 20\%$ of %relative difference	
15	Total no. of elements excluded from QC criterion	
15	>50% of samples below 10x detection limit	
(1)	% duplicates with $\geq 95\%$ samples within $\pm 20\%$ of relative difference $\left(\frac{A}{A+B}\right) \times 100$	10%
(2)	Average of average % relative difference:	14%

A5. Robust Factor Analyses

Collahuasi Rocks

ASSAY	F1	ASSAY	F2	ASSAY	F3	ASSAY	F4	ASSAY	F5
Al2O3_4AWR	0.942	Cd_1FMS	0.731	Zr_4BWR	0.626	TOT_C_4ALC	0.462	S_4ALC	0.778
Co_1FMS	0.939	Pb_1FMS	0.728	Na2O_4AWR	0.530	Ai_100	0.107	TOT_C_4ALC	0.462
CaO_4AWR	0.934	Ag_1FMS	0.628	TOT_C_4ALC	0.304	CaO_4AWR	0.089	Hg_1FMS	0.325
MgO_4AWR	0.934	Zn_1FMS	0.528	P2O5_4AWR	0.172	MgO_4AWR	0.072	K2O_4AWR	0.157
Fe2O3_4AWR	0.907	TOT_C_4ALC	0.424	As_1FMS	0.158	Al2O3_4AWR	0.038	P2O5_4AWR	0.154
P2O5_4AWR	0.899	Cu_1FMS	0.409	Zn_1FMS	0.133	SiO2_4AWR	0.015	As_1FMS	0.133
Ni_1FMS	0.830	Mo_1FMS	0.373	SiO2_4AWR	0.124	P2O5_4AWR	-0.024	Ai_100	0.110
Zn_1FMS	0.581	Zr_4BWR	0.264	Pb_1FMS	0.082	Cd_1FMS	-0.025	Ag_1FMS	0.109
Na2O_4AWR	0.506	Hg_1FMS	0.201	Cd_1FMS	0.069	Ag_1FMS	-0.030	Zr_4BWR	0.067
Cu_1FMS	0.414	Ai_100	0.159	Mo_1FMS	-0.026	Fe2O3_4AWR	-0.043	Fe2O3_4AWR	0.041
Cd_1FMS	0.221	Na2O_4AWR	0.141	CaO_4AWR	-0.038	Na2O_4AWR	-0.062	CaO_4AWR	0.029
Hg_1FMS	0.221	Fe2O3_4AWR	0.122	S_4ALC	-0.039	K2O_4AWR	-0.062	Mo_1FMS	0.009
As_1FMS	0.196	Co_1FMS	0.083	K2O_4AWR	-0.041	Co_1FMS	-0.093	Al2O3_4AWR	0.002
TOT_C_4ALC	0.122	P2O5_4AWR	0.074	Fe2O3_4AWR	-0.051	Zn_1FMS	-0.094	SiO2_4AWR	-0.032
Ag_1FMS	0.025	MgO_4AWR	0.073	Al2O3_4AWR	-0.100	S_4ALC	-0.117	Co_1FMS	-0.033
Mo_1FMS	-0.108	CaO_4AWR	0.061	Co_1FMS	-0.149	Cu_1FMS	-0.141	Cd_1FMS	-0.042
Zr_4BWR	-0.137	Ni_1FMS	0.054	MgO_4AWR	-0.149	Ni_1FMS	-0.210	MgO_4AWR	-0.043
S_4ALC	-0.148	As_1FMS	0.037	Ai_100	-0.177	Hg_1FMS	-0.280	Pb_1FMS	-0.058
Pb_1FMS	-0.162	Al2O3_4AWR	0.027	Ni_1FMS	-0.290	Pb_1FMS	-0.292	Ni_1FMS	-0.065
Ai_100	-0.532	K2O_4AWR	-0.067	Hg_1FMS	-0.340	Zr_4BWR	-0.321	Cu_1FMS	-0.080
K2O_4AWR	-0.816	SiO2_4AWR	-0.079	Ag_1FMS	-0.449	Mo_1FMS	-0.637	Na2O_4AWR	-0.217
SiO2_4AWR	-0.954	S_4ALC	-0.132	Cu_1FMS	-0.620	As_1FMS	-0.729	Zn_1FMS	-0.231

Los Bronces Rocks

ASSAY	F1	ASSAY	F2	ASSAY	F3	ASSAY	F4	ASSAY	F5	ASSAY	F6
SiO2_4AWR	0.973	S_4ALC	0.750	Cd_1FMS	0.814	Zr_4BWR	0.797	Cu_1FMS	0.435	Cu_1FMS	0.319
K2O_4AWR	0.751	As_1FMS	0.688	Pb_1FMS	0.777	Mo_1FMS	0.729	Ni_1FMS	0.391	Ni_1FMS	0.310
Pb_1FMS	0.360	Ni_1FMS	0.528	Zn_1FMS	0.729	K2O_4AWR	0.436	Co_1FMS	0.254	Al2O3_4AWR	0.227
Zr_4BWR	0.343	Co_1FMS	0.245	Ag_1FMS	0.671	P2O5_4AWR	0.340	Ag_1FMS	0.239	Ag_1FMS	0.224
Mo_1FMS	0.210	Ag_1FMS	0.242	Cu_1FMS	0.152	Cu_1FMS	0.325	Ai_100	0.213	MgO_4AWR	0.194
Cd_1FMS	0.073	Cu_1FMS	0.236	As_1FMS	0.142	Ag_1FMS	0.224	K2O_4AWR	0.159	K2O_4AWR	0.108
Hg_1FMS	0.055	MgO_4AWR	0.211	Hg_1FMS	0.113	S_4ALC	0.164	MgO_4AWR	0.140	CaO_4AWR	0.106
S_4ALC	0.053	Mo_1FMS	0.178	K2O_4AWR	0.056	Na2O_4AWR	0.125	CaO_4AWR	0.131	SiO2_4AWR	0.087
Na2O_4AWR	0.036	Pb_1FMS	0.143	Co_1FMS	0.051	Pb_1FMS	0.089	S_4ALC	0.124	Na2O_4AWR	0.065
Ai_100	-0.003	Al2O3_4AWR	0.119	P2O5_4AWR	0.033	SiO2_4AWR	0.087	TOT_C_4ALC	0.099	Mo_1FMS	-0.013
As_1FMS	-0.071	K2O_4AWR	0.107	Mo_1FMS	0.023	TOT_C_4ALC	0.025	Mo_1FMS	0.069	Pb_1FMS	-0.021
TOT_C_4ALC	-0.163	Zn_1FMS	0.096	Na2O_4AWR	0.021	Fe2O3_4AWR	-0.017	Fe2O3_4AWR	0.020	S_4ALC	-0.030
Ag_1FMS	-0.183	Hg_1FMS	0.067	Ai_100	0.016	As_1FMS	-0.042	Cd_1FMS	0.005	As_1FMS	-0.054
Zn_1FMS	-0.253	Ai_100	0.064	S_4ALC	0.015	Hg_1FMS	-0.076	SiO2_4AWR	-0.018	Cd_1FMS	-0.070
Ni_1FMS	-0.455	Na2O_4AWR	0.052	Zr_4BWR	0.015	Cd_1FMS	-0.081	Zr_4BWR	-0.023	Zr_4BWR	-0.083
Cu_1FMS	-0.512	Zr_4BWR	0.017	SiO2_4AWR	0.010	Zn_1FMS	-0.112	Hg_1FMS	-0.055	Fe2O3_4AWR	-0.179
P2O5_4AWR	-0.698	Fe2O3_4AWR	-0.038	Fe2O3_4AWR	0.002	Ni_1FMS	-0.116	Al2O3_4AWR	-0.092	Co_1FMS	-0.180
Al2O3_4AWR	-0.733	SiO2_4AWR	-0.039	Al2O3_4AWR	0.000	CaO_4AWR	-0.126	Zn_1FMS	-0.099	Ai_100	-0.194
Co_1FMS	-0.831	TOT_C_4ALC	-0.067	Ni_1FMS	-0.001	Co_1FMS	-0.158	Pb_1FMS	-0.118	P2O5_4AWR	-0.288
MgO_4AWR	-0.853	CaO_4AWR	-0.099	TOT_C_4ALC	-0.009	MgO_4AWR	-0.242	P2O5_4AWR	-0.211	Zn_1FMS	-0.388
CaO_4AWR	-0.892	Cd_1FMS	-0.152	MgO_4AWR	-0.050	Al2O3_4AWR	-0.348	As_1FMS	-0.369	Hg_1FMS	-0.596
Fe2O3_4AWR	-0.910	P2O5_4AWR	-0.253	CaO_4AWR	-0.070	Ai_100	-0.769	Na2O_4AWR	-0.852	TOT_C_4ALC	-0.794

Collahuasi Soils

ASSAY	F1	ASSAY	F2	ASSAY	F3	ASSAY	F4
Mg_1FMS	0.901	Ca_1FMS	0.270	Mo_1FMS	0.881	Zr_1FMS	0.697
Fe_1FMS	0.854	Na_1FMS	0.264	S_1FMS	0.835	Al_1FMS	0.491
Co_1FMS	0.820	K_1FMS	-0.054	Na_1FMS	0.769	As_1FMS	0.460
P_1FMS	0.754	Hg_1FMS	-0.077	Ni_1FMS	0.432	Cu_1FMS	0.259
Al_1FMS	0.708	Zr_1FMS	-0.111	As_1FMS	0.421	Ni_1FMS	0.250
Ni_1FMS	0.702	Mg_1FMS	-0.134	K_1FMS	0.390	Mo_1FMS	0.114
Ca_1FMS	0.658	Fe_1FMS	-0.136	Ca_1FMS	0.270	Ag_1FMS	0.083
K_1FMS	0.601	Co_1FMS	-0.167	Cd_1FMS	0.253	S_1FMS	-0.008
Hg_1FMS	0.394	S_1FMS	-0.239	Zr_1FMS	0.214	P_1FMS	-0.009
Zn_1FMS	0.309	Ni_1FMS	-0.262	Cu_1FMS	0.156	Mg_1FMS	-0.026
Cu_1FMS	0.273	P_1FMS	-0.285	Ag_1FMS	0.094	Na_1FMS	-0.052
Na_1FMS	0.177	Al_1FMS	-0.327	Mg_1FMS	0.091	Pb_1FMS	-0.081
As_1FMS	0.168	Mo_1FMS	-0.335	Hg_1FMS	0.075	Fe_1FMS	-0.132
Cd_1FMS	0.133	Cd_1FMS	-0.563	Co_1FMS	0.060	Zn_1FMS	-0.175
Pb_1FMS	0.114	As_1FMS	-0.633	P_1FMS	0.036	Co_1FMS	-0.377
Ag_1FMS	0.073	Cu_1FMS	-0.738	Al_1FMS	0.025	K_1FMS	-0.413
S_1FMS	0.066	Ag_1FMS	-0.820	Pb_1FMS	0.004	Ca_1FMS	-0.517
Zr_1FMS	0.048	Zn_1FMS	-0.875	Zn_1FMS	-0.004	Cd_1FMS	-0.581
Mo_1FMS	0.009	Pb_1FMS	-0.912	Fe_1FMS	-0.045	Hg_1FMS	-0.778

A6. Robust Correlation Analysis Matrices

Collahuasi Rocks

	Ag_1FMS	Ai_100	Al2O3_4AWR	As_1FMS	CaO_4AWR	Cd_1FMS	Co_1FMS	Cu_1FMS	Fe2O3_4AWR	Hg_1FMS	K2O_4AWR	MgO_4AWR	Mo_1FMS	Na2O_4AWR	Ni_1FMS	P2O5_4AWR	Pb_1FMS	S_4ALC	SiO2_4AWR	TOT_C_4ALC	Zn_1FMS	Zr_4BWR
Ag_1FMS	1.000	0.104	0.072	-0.010	0.067	0.301	0.103	0.453	0.168	0.270	-0.066	0.084	0.196	-0.077	0.144	0.055	0.333	0.046	-0.150	0.063	0.269	-0.003
Ai_100	0.104	1.000	-0.419	-0.078	-0.512	-0.044	-0.423	-0.134	-0.393	-0.050	0.436	-0.410	0.046	-0.328	-0.384	-0.416	0.056	0.070	0.423	0.016	-0.238	0.014
Al2O3_4AWR	0.072	-0.419	1.000	0.119	0.893	0.230	0.887	0.447	0.855	0.212	-0.726	0.901	-0.086	0.409	0.768	0.850	-0.140	-0.141	-0.952	0.080	0.531	-0.174
As_1FMS	-0.010	-0.078	0.119	1.000	0.127	0.169	0.224	0.045	0.170	0.159	-0.131	0.127	0.284	0.157	0.271	0.215	0.237	0.051	-0.178	-0.066	0.185	0.129
CaO_4AWR	0.067	-0.512	0.893	0.127	1.000	0.290	0.856	0.388	0.828	0.172	-0.786	0.893	-0.074	0.392	0.737	0.830	-0.105	-0.133	-0.894	0.182	0.506	-0.202
Cd_1FMS	0.301	-0.044	0.230	0.169	0.290	1.000	0.239	0.323	0.223	0.149	-0.280	0.255	0.214	0.227	0.210	0.224	0.436	-0.079	-0.228	0.230	0.467	0.109
Co_1FMS	0.103	-0.423	0.887	0.224	0.856	0.239	1.000	0.515	0.875	0.283	-0.701	0.927	-0.007	0.396	0.873	0.823	-0.064	-0.174	-0.908	0.067	0.621	-0.165
Cu_1FMS	0.453	-0.134	0.447	0.045	0.388	0.323	0.515	1.000	0.442	0.361	-0.357	0.458	0.207	0.021	0.556	0.297	0.192	-0.076	-0.481	-0.040	0.413	-0.229
Fe2O3_4AWR	0.168	-0.393	0.855	0.170	0.828	0.223	0.875	0.442	1.000	0.224	-0.671	0.870	-0.039	0.349	0.768	0.855	-0.035	-0.160	-0.944	0.112	0.553	0.026
Hg_1FMS	0.270	-0.050	0.212	0.159	0.172	0.149	0.283	0.361	0.224	1.000	-0.142	0.207	0.157	0.089	0.288	0.189	0.067	0.020	-0.227	0.068	0.085	-0.024
K2O_4AWR	-0.066	0.436	-0.726	-0.131	-0.786	-0.280	-0.701	-0.357	-0.671	-0.142	1.000	-0.722	0.080	-0.630	-0.662	-0.644	0.107	0.172	0.724	-0.088	-0.471	0.202
MgO_4AWR	0.084	-0.410	0.901	0.127	0.893	0.255	0.927	0.458	0.870	0.207	-0.722	1.000	-0.104	0.317	0.802	0.810	-0.095	-0.215	-0.923	0.125	0.572	-0.218
Mo_1FMS	0.196	0.046	-0.086	0.284	-0.074	0.214	-0.007	0.207	-0.039	0.157	0.080	-0.104	1.000	0.012	0.072	-0.058	0.372	0.011	0.044	-0.018	0.112	0.247
Na2O_4AWR	-0.077	-0.328	0.409	0.157	0.392	0.227	0.396	0.021	0.349	0.089	-0.630	0.317	0.012	1.000	0.293	0.497	0.017	-0.184	-0.358	0.116	0.487	0.189
Ni_1FMS	0.144	-0.384	0.768	0.271	0.737	0.210	0.873	0.556	0.768	0.288	-0.662	0.802	0.072	0.293	1.000	0.641	-0.048	-0.134	-0.819	-0.027	0.529	-0.227
P2O5_4AWR	0.055	-0.416	0.850	0.215	0.830	0.224	0.823	0.297	0.855	0.189	-0.644	0.810	-0.058	0.497	0.641	1.000	-0.098	-0.061	-0.867	0.200	0.548	0.086
Pb_1FMS	0.333	0.056	-0.140	0.237	-0.105	0.436	-0.064	0.192	-0.035	0.067	0.107	-0.095	0.372	0.017	-0.048	-0.098	1.000	-0.034	0.079	0.144	0.299	0.256
S_4ALC	0.046	0.070	-0.141	0.051	-0.133	-0.079	-0.174	-0.076	-0.160	0.020	0.172	-0.215	0.011	-0.184	-0.134	-0.061	-0.034	1.000	0.150	0.027	-0.200	-0.004
SiO2_4AWR	-0.150	0.423	-0.952	-0.178	-0.894	-0.228	-0.908	-0.481	-0.944	-0.227	0.724	-0.923	0.044	-0.358	-0.819	-0.867	0.079	0.150	1.000	-0.110	-0.549	0.129
TOT_C_4ALC	0.063	0.016	0.080	-0.066	0.182	0.230	0.067	-0.040	0.112	0.068	-0.088	0.125	-0.018	0.116	-0.027	0.200	0.144	0.027	-0.110	1.000	0.123	0.055
Zn_1FMS	0.269	-0.238	0.531	0.185	0.506	0.467	0.621	0.413	0.553	0.085	-0.471	0.572	0.112	0.487	0.529	0.548	0.299	-0.200	-0.549	0.123	1.000	0.158
Zr_4BWR	-0.003	0.014	-0.174	0.129	-0.202	0.109	-0.165	-0.229	0.026	-0.024	0.202	-0.218	0.247	0.189	-0.227	0.086	0.256	-0.004	0.129	0.055	0.158	1.000

Los Bronces Rocks

	Ag_1FMS	Ai_100	Al2O3_4AWR	As_1FMS	CaO_4AWR	Cd_1FMS	Co_1FMS	Cu_1FMS	Fe2O3_4AWR	Hg_1FMS	K2O_4AWR	MgO_4AWR	Mo_1FMS	Na2O_4AWR	Ni_1FMS	P2O5_4AWR	Pb_1FMS	S_4ALC	SiO2_4AWR	TOT_C_4ALC	Zn_1FMS	Zr_4BWR
Ag_1FMS	1.000	-0.115	0.107	0.126	0.104	0.320	0.195	0.514	0.107	0.012	0.045	0.172	0.157	-0.074	0.267	0.037	0.414	0.241	-0.135	-0.101	0.367	0.050
Ai_100	-0.115	1.000	0.234	0.008	0.001	0.046	0.247	-0.133	0.115	0.099	-0.268	0.174	-0.405	-0.235	0.066	-0.135	-0.108	-0.058	-0.093	0.048	0.179	-0.549
Al2O3_4AWR	0.107	0.234	1.000	0.070	0.723	-0.033	0.609	0.300	0.561	-0.061	-0.630	0.729	-0.307	0.057	0.457	0.255	-0.279	0.010	-0.757	-0.046	0.149	-0.497
As_1FMS	0.126	0.008	0.070	1.000	-0.028	0.036	0.146	0.014	0.099	0.003	-0.005	0.152	0.015	0.133	0.188	0.004	0.243	0.260	-0.112	-0.041	0.197	0.009
CaO_4AWR	0.104	0.001	0.723	-0.028	1.000	-0.064	0.678	0.404	0.754	-0.088	-0.734	0.813	-0.256	-0.230	0.443	0.509	-0.375	-0.090	-0.884	0.114	0.077	-0.466
Cd_1FMS	0.320	0.046	-0.033	0.036	-0.064	1.000	-0.031	-0.011	-0.053	0.113	0.043	-0.136	-0.001	-0.008	-0.099	-0.016	0.526	-0.018	0.055	0.063	0.511	-0.016
Co_1FMS	0.195	0.247	0.609	0.146	0.678	-0.031	1.000	0.496	0.802	0.019	-0.619	0.780	-0.221	-0.221	0.604	0.446	-0.273	0.094	-0.840	0.278	0.368	-0.370
Cu_1FMS	0.514	-0.133	0.300	0.014	0.404	-0.011	0.496	1.000	0.378	-0.143	-0.144	0.485	0.180	-0.184	0.563	0.217	-0.092	0.195	-0.422	-0.099	0.023	0.009
Fe2O3_4AWR	0.107	0.115	0.561	0.099	0.754	-0.053	0.802	0.378	1.000	-0.001	-0.678	0.737	-0.224	-0.128	0.274	0.717	-0.331	-0.053	-0.919	0.194	0.308	-0.286
Hg_1FMS	0.012	0.099	-0.061	0.003	-0.088	0.113	0.019	-0.143	-0.001	1.000	-0.078	-0.097	0.004	0.083	-0.111	0.052	0.121	-0.036	0.002	0.265	0.188	-0.012
K2O_4AWR	0.045	-0.268	-0.630	-0.005	-0.734	0.043	-0.619	-0.144	-0.678	-0.078	1.000	-0.652	0.464	-0.067	-0.238	-0.421	0.336	0.150	0.725	-0.220	-0.213	0.643
MgO_4AWR	0.172	0.174	0.729	0.152	0.813	-0.136	0.780	0.485	0.737	-0.097	-0.652	1.000	-0.319	-0.170	0.675	0.369	-0.313	0.040	-0.858	-0.033	0.129	-0.479
Mo_1FMS	0.157	-0.405	-0.307	0.015	-0.256	-0.001	-0.221	0.180	-0.224	0.004	0.464	-0.319	1.000	0.086	-0.091	0.015	0.178	0.242	0.259	-0.037	-0.122	0.522
Na2O_4AWR	-0.074	-0.235	0.057	0.133	-0.230	-0.008	-0.221	-0.184	-0.128	0.083	-0.067	-0.170	0.086	1.000	-0.242	0.100	0.092	-0.028	0.090	-0.044	0.044	0.081
Ni_1FMS	0.267	0.066	0.457	0.188	0.443	-0.099	0.604	0.563	0.274	-0.111	-0.238	0.675	-0.091	-0.242	1.000	-0.054	-0.120	0.266	-0.433	-0.122	0.038	-0.223
P2O5_4AWR	0.037	-0.135	0.255	0.004	0.509	-0.016	0.446	0.217	0.717	0.052	-0.421	0.369	0.015	0.100	-0.054	1.000	-0.205	-0.137	-0.642	0.223	0.296	0.068
Pb_1FMS	0.414	-0.108	-0.279	0.243	-0.375	0.526	-0.273	-0.092	-0.331	0.121	0.336	-0.313	0.178	0.092	-0.120	-0.205	1.000	0.078	0.346	-0.031	0.452	0.209
S_4ALC	0.241	-0.058	0.010	0.260	-0.090	-0.018	0.094	0.195	-0.053	-0.036	0.150	0.040	0.242	-0.028	0.266	-0.137	0.078	1.000	0.029	-0.047	0.079	0.109
SiO2_4AWR	-0.135	-0.093	-0.757	-0.112	-0.884	0.055	-0.840	-0.422	-0.919	0.002	0.725	-0.858	0.259	0.090	-0.433	-0.642	0.346	0.029	1.000	-0.227	-0.269	0.373
TOT_C_4ALC	-0.101	0.048	-0.046	-0.041	0.114	0.063	0.278	-0.099	0.194	0.265	-0.220	-0.033	-0.037	-0.044	-0.122	0.223	-0.031	-0.047	-0.227	1.000	0.268	-0.029
Zn_1FMS	0.367	0.179	0.149	0.197	0.077	0.511	0.368	0.023	0.308	0.188	-0.213	0.129	-0.122	0.044	0.038	0.296	0.452	0.079	-0.269	0.268	1.000	-0.086
Zr_4BWR	0.050	-0.549	-0.497	0.009	-0.466	-0.016	-0.370	0.009	-0.286	-0.012	0.643	-0.479	0.522	0.081	-0.223	0.068	0.209	0.109	-0.029	-0.086	1.000	

Collahuasi Soils

	Ag_1FMS	Al_1FMS	As_1FMS	Ca_1FMS	Cd_1FMS	Co_1FMS	Cu_1FMS	Fe_1FMS	Hg_1FMS	K_1FMS	Mg_1FMS	Mo_1FMS	Na_1FMS	Ni_1FMS	P_1FMS	Pb_1FMS	S_1FMS	Zn_1FMS	Zr_1FMS
Ag_1FMS	1.000	0.310	0.595	-0.145	0.297	0.109	0.635	0.157	0.016	0.143	0.229	0.338	-0.003	0.238	0.355	0.707	0.227	0.725	0.124
Al_1FMS	0.310	1.000	0.563	0.075	-0.004	0.428	0.554	0.533	-0.021	0.318	0.676	0.207	-0.058	0.709	0.570	0.325	0.221	0.399	0.344
As_1FMS	0.595	0.563	1.000	-0.165	0.172	0.095	0.680	0.134	-0.176	0.105	0.270	0.624	0.124	0.540	0.336	0.523	0.521	0.503	0.393
Ca_1FMS	-0.145	0.075	-0.165	1.000	0.321	0.661	-0.080	0.566	0.598	0.669	0.618	0.053	0.502	0.335	0.430	-0.111	0.132	0.090	-0.240
Cd_1FMS	0.297	-0.004	0.172	0.321	1.000	0.500	0.293	0.310	0.504	0.385	0.171	0.332	0.059	0.298	0.195	0.595	0.318	0.639	-0.078
Co_1FMS	0.109	0.428	0.095	0.661	0.500	1.000	0.274	0.840	0.664	0.603	0.699	0.094	0.125	0.583	0.607	0.267	0.163	0.426	-0.102
Cu_1FMS	0.635	0.554	0.680	-0.080	0.293	0.274	1.000	0.231	0.023	0.153	0.386	0.420	-0.014	0.469	0.378	0.615	0.286	0.641	0.254
Fe_1FMS	0.157	0.533	0.134	0.566	0.310	0.840	0.231	1.000	0.414	0.475	0.701	0.013	0.108	0.556	0.611	0.258	0.074	0.403	0.060
Hg_1FMS	0.016	-0.021	-0.176	0.598	0.504	0.664	0.023	0.414	1.000	0.549	0.378	0.008	0.092	0.158	0.266	0.134	0.155	0.285	-0.464
K_1FMS	0.143	0.318	0.105	0.669	0.385	0.603	0.153	0.475	0.549	1.000	0.607	0.310	0.358	0.454	0.462	0.161	0.360	0.289	-0.204
Mg_1FMS	0.229	0.676	0.270	0.618	0.171	0.699	0.386	0.701	0.378	0.607	1.000	0.134	0.225	0.675	0.694	0.217	0.155	0.425	-0.049
Mo_1FMS	0.338	0.207	0.624	0.053	0.332	0.094	0.420	0.013	0.008	0.310	0.134	1.000	0.522	0.510	0.144	0.280	0.807	0.257	0.245
Na_1FMS	-0.003	-0.058	0.124	0.502	0.059	0.125	-0.014	0.108	0.092	0.358	0.225	0.522	1.000	0.295	0.134	-0.147	0.420	-0.104	0.164
Ni_1FMS	0.238	0.709	0.540	0.335	0.298	0.583	0.469	0.556	0.158	0.454	0.675	0.510	0.295	1.000	0.568	0.312	0.469	0.400	0.369
P_1FMS	0.355	0.570	0.336	0.430	0.195	0.607	0.378	0.611	0.266	0.462	0.694	0.144	0.134	0.568	1.000	0.339	0.178	0.481	-0.077
Pb_1FMS	0.707	0.325	0.523	-0.111	0.595	0.267	0.615	0.258	0.134	0.161	0.217	0.280	-0.147	0.312	0.339	1.000	0.194	0.846	0.122
S_1FMS	0.227	0.221	0.521	0.132	0.318	0.163	0.286	0.074	0.155	0.360	0.155	0.807	0.420	0.469	0.178	0.194	1.000	0.190	0.092
Zn_1FMS	0.725	0.399	0.503	0.090	0.639	0.426	0.641	0.403	0.285	0.289	0.425	0.257	-0.104	0.400	0.481	0.846	0.190	1.000	0.024
Zr_1FMS	0.124	0.344	0.393	-0.240	-0.078	-0.102	0.254	0.060	-0.464	-0.204	-0.049	0.245	0.164	0.369	-0.077	0.122	0.092	0.024	1.000